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Some Neoteric Tin Complexes Used in Biological Properties

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Abstract Tin has a variety of advantageous biological effects. The majority of tin complexes are effective against a wide range of different disorders, including convulsion, tumor, cancer, malaria, tuberculosis, and diabetes. The majority of the tin complex exhibits drug-like antibacterial and antifungal properties. Tin complexes have greater activity than free ligands like macrocyclic and Schiff bases. A new series of tin (II) and tin (IV) complexes were formed as a result of n - heterocyclic Schiff base ligand. Three tin (IV) complexes, H-ClQ=5, 7-dichloro-8-hydroxylquinoline, H-BrQ=5, 7-dibromo-8-hydroxylquinoline, and H-ClIQ=5-chloro-7-iodo-8-hydroxylquinoline, were created. There in vitro information about the condition against the cell lines BEL7404, SKOV-3, NCI-H460, and HL-770 Having IC50 values that range from 20 nm to 5.11 mM, the compound exhibits strong anti-proliferative action against the investigated cell lines. Most complexes showed significantly increased cytotoxicity as compared to 5, 7-dihalo-8-quinolinol (except 2 against SKOV-3 and NCI-H460). Additionally, they showed some selective cytotoxicity that favoured the tested tumor cells over the healthy HL-7702 cells from the human liver. Complexes 1-3 bind DNA more firmly compared to their quinolinol ligands. Macrocyclic molecules, which include porphyrin rings connected to metal ions in cytochromes, heamoglobin, and chlorophyll, may have significant effects on the biochemistry of biological systems. The biological applications of complexes of transition metals with ligands have been the subject of extensive research. The most likely binding mode for the aggregates with their quinolinol ligands is intercalation. The significance of tin applications in biological processes is explained in this review paper.

Keywords: *tin complexes, biological activity, macrocyclic ligands and schiff base ligands*

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1. Introduction

The oxidation states 0, +2, and +4 as well as their electronic configuration [Kr], 5s2, and 5p2 are all demonstrated by the metal tin. Tin complexes are used in paints, plastic pipes, toothpaste, soaps, food additives, food packaging, textiles, as well as foods and beverages [1]. Due to their limited absorption, organotin, inorganic tin, and its salts are not very poisonous. However, inorganic tin poisoning in mammals can cause systemic and local symptoms like vomiting, diarrhoea, eye and nose irritation, ataxia, paralysis, and growth retardation. [2,3]. While inorganic tin compounds are hazardous, organotin itself is not toxic [4]. Thiosemicarbazones [5] and other transition metal complexes [6] show various therapeutic qualities in medicinal chemistry in recent years [7]. As a result of their pharmacological capabilities, which include antiviral [8], antibacterial [9], antifungal [10], antiphrastic [11], antitumor [12], anticancer [13]. A recent Mn(II), Fe(II), and Co(II). While organic tin compounds and elemental tin are not hazardous, some species of organic tin compounds are. In general, monosubstituted tin complexes [R-Sn-X3] are less dangerous than disubstituted tin complexes [R2-Sn-X2] and trisubstituted tin complexes [R3-Sn-X] due to the higher number of alkyl groups [14]. The charge transfer band in the tin complexes causes them to exhibit sharp bands in the 240-260 nanometer range [15]. Because the tin element's 5d-orbital is completely vacant, Sn—N bonds are formed by the donation of a lone pair of electrons from the ligands' azomethinenitrogen [16]. Biologically active organotin compounds have the general formula $Rn\text{-}Sn\text{-}X_{4\text{-}n}$ [17]. Organotin and inorganic tin compounds are the two main categories of tin compounds. It displays several characteristics. 2- (4methoxybenzylidene amino) Butanoic acid (4-methyl-thio) and 3mercapto -2-(4 methoxybenzylidene amino) The Schiff base ligand complexes with 4-propanoic acid ligands triggered by tin elements have greater antimicrobial activities than the other Schiff base ligands. Another sciff base such as their the condensation of 2-amino phenol with 4-hydroxy benzaldehyde yields Sn(II) ions with tridentate N,O containing Schiff base ligand 2-(4-hydroxybenzylidene) amino phenol, which has been synthesised and variously

characterised. There has been evidence of moderate to strong microbial activity for the Schiff base Sn and various distinct metal complexes. [45]

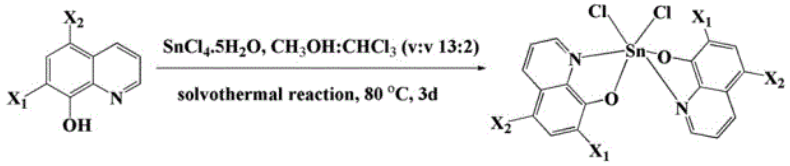
Due to interaction of metal ions with large Schiff base ligands, tin complexes improve its lipophilic characteristic with bacterial lipoid layer and reduce the polarity of metal ions due to overlaps among ligand and metal orbital angular momentum (increase the delocalization of +ve change). Tin complexes, such as 2-(4-methoxybenzylideneamino)-4-methyl-thio) butanoic acid and 3-mercapto-2-(4-methoxybenzylideneamino)-4-propanoicacid, show greater inhibitory efficacy than the free ligand against all microorganisms. Tin complexes boost the antibacterial activity when they are formed, and so this complex is being used in drug design and its applications [18]. Complexes created when tin coordinates with synthesized ligand are particularly helpful in biological function. Klebsiella pneumoniae and Escherichia coli are two examples of gram-negative bacteria that are particularly susceptible to the tin complex $[Sn(HNCA)Cl_2(H_2O)_2]$, while Staphylococcus aureus, Staphylococcus epidermidis, and Bacillus subtilis are among the gram-positive bacteria that are particularly susceptible to the tin complex [19]. Aspergillus niger, Aspergillus flavus, and Alternaria solani are all susceptible to the antifungal action of the complexes $[Sn(HNOT)Cl_2(H_2O)_2]$ and $[Sn(HNPA)Cl_2(H_2O)_2]$ [20]. The majority of the tin complexes were tested against the gram-positive bacteria Pseudomonas phaseolicoles and Escherichia coli. Fusarium oxysporum and Alternaria alternaria make up the majority of the pathogenic fungus used in these investigations [21]. According to Har Lal Singh et al. [22], tricyclohexyltin alaninate complex is highly effective against fungicide and bactericide for seeds and plants [23] Schiff bases have anticarcinogenic [24], antimicrobial [25,46,50], and antifungal [47], antitumor [26] effects when metal coordinate with amino acid. Biochemicals are flavonoids. Due to their biological and pharmacological properties, which include circulatory protective, anticancer potential [48], antiulcer, antiallergic, antiviral, anti-inflammatory, and antioxidant properties [51], it is beneficial to human health.

2. Tin Metal Complexes' Involvement in Flavonoids Compounds

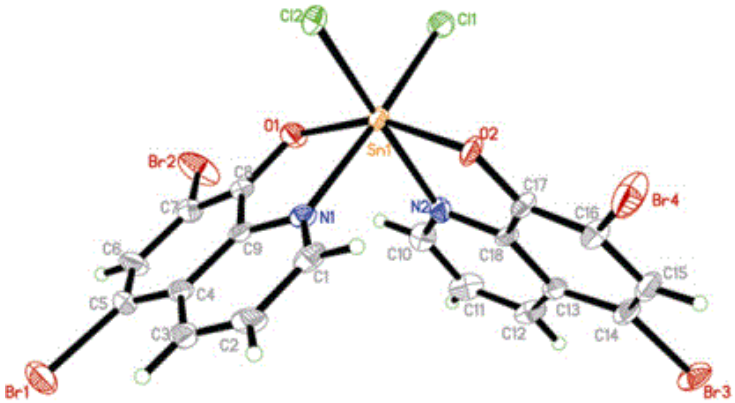
Flavonoids (2-phenyl-benzo-γ-pyrones) are a large group of polyphenolic natural compounds that are distributed in plant-foods. Flavonoids are bio chemicals. Which favorable for human health due to their biological and pharmacological properties, including cardiovascular protection, anticancer, antiulcer, antiallergic, antioxidant, antiviral and anti-inflammatory potentials. Quercetin (Q;3,3',4',5,7-pentahydroxyflavone) is one of the most common flavonoids present in nature. Flavonoids are important natural antioxidants and free radical scavengers and strong metal chelators. Chelating property of common flavonoids exist in many fruits and vegetables, canned foods and beverages, against toxic tin cations [Sn (II)], and investigation of antioxidant properties of Chelation. The capacity of flavonoids to act as antioxidants depends on their molecular structure [27]. Chelation therapy is the preferred method for reducing the heavy metal induced toxicity chelating agent form complex structure with toxic metal ions which are easily excreted from the body [28]. Platinum drugs [cisplatin] used in cancer chemotherapy and cisplatin shows antiproliferative properties [29]. The many efforts that initially focused on the evaluation of platinum metal based agents. Organotin (IV) complexes have interesting activities, they can leads to potential environmental pollution. The inorganic tin (IV) complexes have been relatively overlooked. Tin (II) complexes were screened for their antibacterial activity against gram -ve *(Escherichia coli and Proteus milamilis)* and gram +ve *(Staphylococcus aureus and Bacillus thurdingiensis)* bacterial stains and their activity determined by using the inhibition Zone Technique. Most of the tin complexes show antifungal activity against *Aspergillus flavus*, *Fusarium oxysporum* and *Aspergillus niger* they are detected by the Radial Growth Method [30]. The tin compound $SnCl_2.C_{34}H_{32}N_4$ gives sharp signal at δ-576 ppm in ^{119}Sn NMR spectrum, below the reported value for tri-coordinated hydrated tin (II) chloride. But in case of four coordination number of tin complexes show squar pyramidal geometry. The tin (IV) complexes $Me_2SnCl_2.C_{34}H_{32}N_4$ sharp signal at δ-250 ppm in the ^{119}Sn NMR spectrum. It shows six coordination number and octahedral geometry [31]. Flavonoids are largest natural polyphenolic compounds. The flavonoid is derived from Latin word 'Flavus' means yellow, but some flavonoids are purple, white, blue, red in colour. It is discovered with vitamin C. Flavonoids are containing over 8,000 varieties. Their structure is characterized by three carbon chains (C6-C3-C6) system joined with two phenyl rings. In structure C_3 is an aliphatic chain and two C6 group are substituted benzene rings, it contain a pyranone ring. Heterocyclic compounds are widely studies in drug discovery and development due to their activities. Such as clioquinol (5-chloro-7- iodoquinolin - 8-ol, an 8-hydroxyquinoline derivative) has antitumor activity in vitro and in vivo clioquinol was previously used as an antibiotic and intestinal amebiasis and studied in the clinical trials for Alzheimer's disease. The three dihalo - substitutedquinolonetin (IV) complexes against three selectedtumorcell lines and the normal human liver HL-7702 [32].

The Sn (IV) atom in complex 2 is chelated by two substituted quinoline-8-plate anions and coordinated by two chlorides. The bischelated Sn atom in complex 2 contain a distorted octahedral environment with cis-Cl_2, cis-N_2 and trans-O_2, complex 1 is similar to complex 1, $Sn(ampH_2)_2Cl_2$ ($ampH_3$ = aminophenol), cis-dichlorobis (8-hydroxyquinoline)tin(IV) and dichlorobis (2- methylquinolin-8-olato-k^2 N,O) tin(IV). The octahedral coordination is distorted with angles in the ranges 77.2- 100.59° and 157.2-172.5°. The cytotoxicity of the ligands H-ClQ, H-BrQ, H-ClIQ and the complexes 1-3 were evaluated by MTT assay on BEL7404, SKOV-3, NCI-H460 and HL-7702 cell lines. Each chemical was tested for cytotoxicity against tumour cells at a dosage of 2x10-5 mol/L for 48 hours. The compounds demonstrated different antitumor activities and selectivity. The inhibition rates of the complexes 1-3 for all tested tumor cell lines (BEL7404, SKOV-3 and NCI-H460) were all >90% and enhanced than their corresponding H-ClQ, H-BrQ and

H-ClIQ ligands. There are two new organotin compounds such as triphenyl-4,6-diamine-pyrimidine2-thione-tin(IV) (1) and triphenyl-imidazoline-2-thione-chlorotin(IV) (2), can been synthesized as well as their cytotoxic activities have been tested against certain cancer cell lines. It so there are the largest anticancer activity has been found for $[R_2Sn(IV)]^{2+}$ compounds, in particular for $[Et_2Sn(IV)]^{2+}$ and $[Ph_2Sn(IV)]^{2+}$(reported on the Anita M. Grześkiewicz et al. [33]). The cytotoxicities of complexes 1-3 are more sensitive against BEL7404 (IC_{50}= 0.27-544 μM) than cisplatin and 13-cis-retinoylferrocence derivatives (IC_{50}= 22.3- 42.6μM). Which is similar to the dihalo-substituted 8-quinolinolato lanthanide complexes such as $[Gd(BrQ)_3(H_2O)_2].1.33EtOH\ 0.33H_2O$, $[Dy(ClQ)_3(H_2O)_2].1.33EtOH\ 0.33H_2O$ and $[Er(ClQ)_3(H_2O)_2].1.33EtOH\ 0.33H_2O$, compared with their corresponding H-ClQ and H-ClIQ ligands. The cytotoxicities of complexes 1and 3 against BEL7404 show a 24 and 60- fold increases. Toward SKOV-3, the complexes 1and 3 have lower IC_{50} values than the free H-ClQ and H-ClIQ ligands, and then complex 2 shows a higher IC_{50} value than the H-BrQ ligand. The CI_{50} value of complex 3 for SKOV-3 reached 38 nM, this complex is an approximately 94-fold increases compared with the free H-ClIQ ligand. Similarly, for the NCI- H460 tumor cell lines, complexes 1 and 3 show lower IC_{50} values than the free H-ClQ and H-ClIQ ligands whereas complex 2 shows a higher IC_{50} value than H-BrQ. The IC_{50} value of complex 3 against NCI-H460 reaches 20 nM, which is an approximately 2038-fold increases compared with the free H-ClIQ ligand. The complexes 1-3 exhibit stronger cytotoxicities than cisplatin. In case of normal liver cell HL-7702, the cytotoxicities of complex 1 toward the BEL7404 and NCI-H460 tumor cell lines are enhanced by 1.7 and 48.5 times, in complex 1 has certain selectivity toward the BEL7404 and NCI-H460 tumor cell lines when compared with the normal liver cell HL-7702.The combination of the dihalo-substituted 8-hydroxylquinolines with tin (IV) may generate a synergistic effect, and the halogen atoms attached to the 8 hydroxylquinolines may contribute to the high cytotoxicities of the complexes. The triphenyltin (IV) complexes with 2-thiobarbituric acid have IC_{50} values of 0.06-0.2 μM toward various tumor cell lines and the tricyclohexyltin (IV) complexes contain IC_{50} values of0.15-1.41 Mn for a number of human tumor cell lines. Therefore, the inorganic tin (IV) complexes 1-3 are potential chemotherapeutic candidates avoidthe pollution problem of the organotin drugs.



X_1=X_2=Cl for complex 1; X_1=X_2= Br for complex 2; X_1=I, X_2=Cl for Complex 3



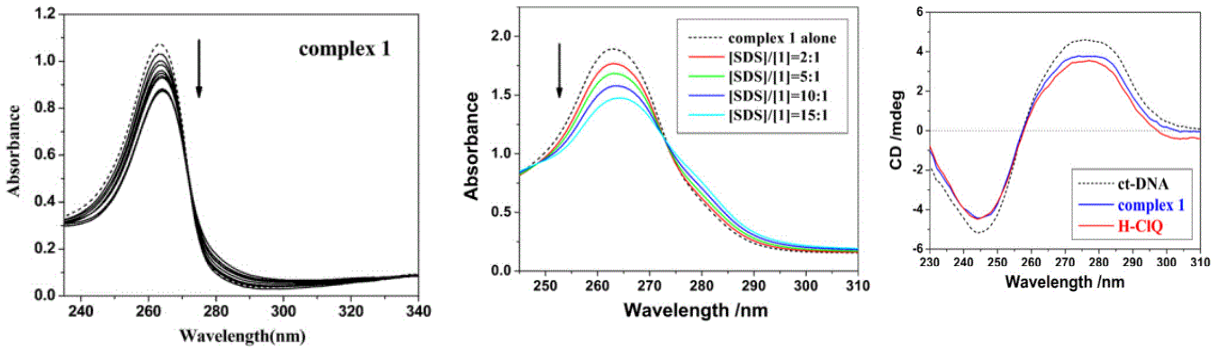


Figure 1. a) Synthetic route for complexes, b) ORTEP drawing of the complex, c) CD spectra of ct-DNA, d) UV-Vis absorption spectra of complex 1 in the absence (dashed line —) and presence (solid lines) of SDS with increasing, e) 5. Fluorescence emission spectra of GelRed bound with ct-DNA

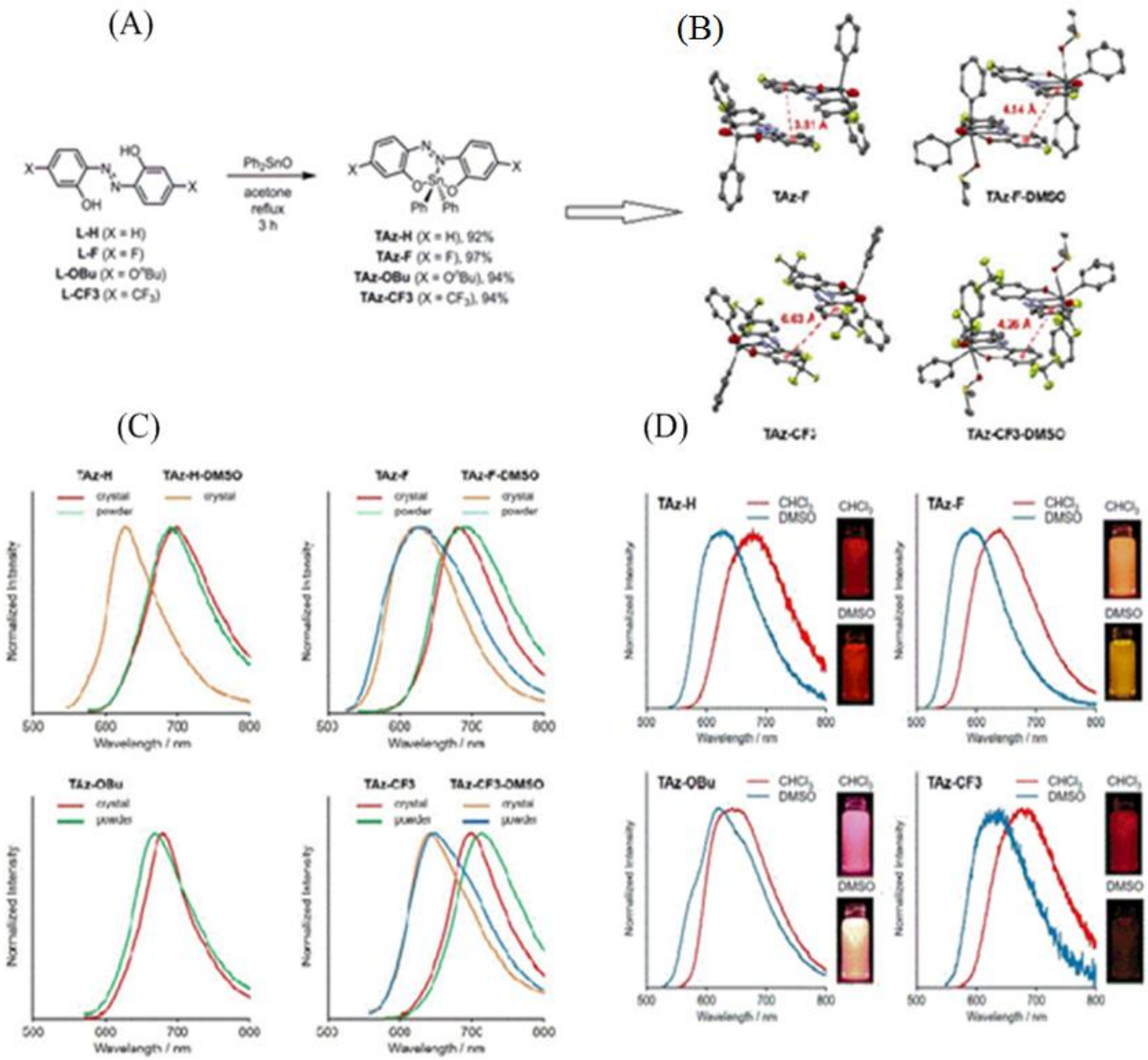


Figure 2. a) Synthesis of TAz complex from each ligand, b) the nearest two benzene rings' distances are shown in the crystal packing structures of TAz-F and TAz-F-DMSO, as well as TAz-CF3 and TAz-CF_3-DMSO, c) wavelengths of the absorption maxima under solution circumstances stimulated the photoluminescence spectra of TAz-H, TAz-F, TAz-OBu, and TAz-CF_3 in the solid state

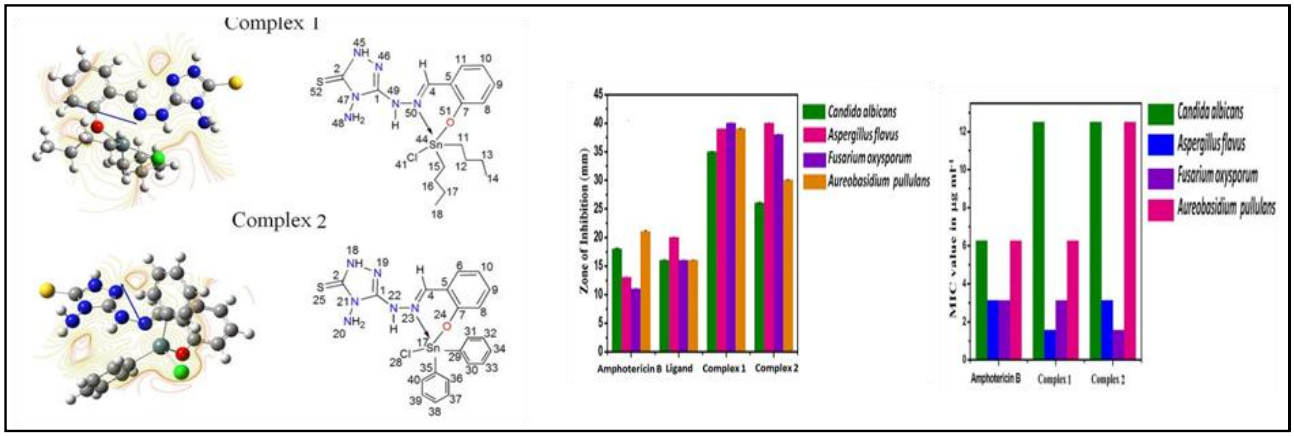


Figure 3. a) Cytotoxicities than 5, 7- dihalo-8-quinolinol ligand toward the tumor cell line. They show selective cytotoxicity favour the tested tumor cell lines of the human liver HL-7702 cells. The binding property of complex 1-3 to DNA are investigated by various method and comparative analysis of zone of inhibition (in mm) at 25 µg ml−1 concentration of HL and it's both diorganotin(IV) complexes against chosen fungal strains and analysis of MIC of Schiff base HL against chosen fungal strains.

Table 1. List of Tin metal complexes with enhance anti therapeutic effect and method

S. No.	Tin metal complexes	Anti activity	Technique/ Method	Reference
1.	$Bu_2Sn(C_{13}H_{11}N_2O_3S)_2$ $Bu_2Sn(C_{18}H_{15}N_4O_3S)_2$ $Bu_2Sn(C_{17}H_{13}N_2O_3S)_2$ $Bu_2Sn(C_{22}H_{17}N_4O_3S)_2$ $Bu_2Sn(C_{14}H_{13}N_2O_3S)_2$ $Bu_2Sn(C_{19}H_{17}N_4O_3S)_2$	Antibacterial & Antifungal	By paper disc diffusion Method. By radial growth method.	A.K. Varshney et al. [35]
2.	[Sn $Me(CO_2Me)_2$] Me $Sn(CH_2\ CH_2\ CH_2)_3N$ $Me_2\ Sn(CH_2CH_2CH_2)_2NMe$ $Me_3SnCF_3.P(NMe_2)_3$	Antitumor	In vitro MTT spectroscopic method	L. Pellerito et al. [36]
3.	N,N-bis[(R)-1-benzyl-2 ethoxyethane]tin(IV) N,N-bis[(S)-1-benzyl-2-ethoxyethane]tin(IV) $[CuSn_2(Trp)]$	Antitumor	By MTT	C. Pettinari et al. [37]
4.	$R_3Sn(\ C_{11}\ H_{12}NO_4)$ $R_2Sn(\ C_{11}\ H_{12}NO_4)_2$ $R_3Sn(\ C_{11}\ H_{12}NO_4)$(2,2-bipyridyl) $R_3Sn(\ C_{11}\ H_{12}NO_4)$ (1,10- Phenanthroline)	Antitumor Antimicrobial Cytotoxicity activity Anti leishmanial activity	By using the potato disc bio array technique	M. Sirajuddin et al. [38]
5.	$[(CH_3)_2Sn\ (C_{21}H_{17}N_4O_2S_2)\ Cl]$ $[(CH_3)_2Sn\ (C_{21}H_{17}N_3S_2)\ Cl_2]$ $[(CH_3)_2Sn(C_{19}H_{15}N_3O_2S)Cl]$ $[(CH_3)_2Sn\ (C_{19}H_{15}N_4S)\ Cl_2]$	Antibacterial And Antifungal activity	In vitro by agar plate technique.	R.V. Singh et al. [39]
6.	$[Sn\ \{S_2CN(CH_2)_4\}_2Cl_2]$ $[Sn\ \{S_2CN(CH_2)_4\}_2Ph_2]$ $[Sn\ \{S_2CN(CH_2)_4\}_2Ph_3]$ $[Sn\ \{S_2CN(CH_2)_4\}_2n\text{-}Bu_2]$ $[Sn\ \{S_2CN(CH_2)_4\}_2Cy_3]$ $[Sn\ \{S_2CN(C_2\ H_5)_2\}Cl_2]$ $[Sn\ \{S_2CN(C_2\ H_5)_2\}_3Ph]$ $[Sn\ \{S_2CN(C_2\ H_5)_2\}Ph_2]$ $[Sn\ \{S_2CN(C_2\ H_5)_2\}Cy_3]$	Antifungal Activity	By DNA integrity assays. Yeast cell viability	D.C. Menzes et al. [40]
7.	$[R_2\ Sn(C_{16}H_{13}NO_2)]$ $[n\text{-}Bu_2Sn(\ C_9H_8N_3O_3)\ (H_2O)]_2$	Antifungal & Antibacterial	In vitro (ligands have been listed against the U937 human Leukemic cell lines), Agar dilution method.	D. Kumar et al. [41]
8.	$[(CH_3)_2Sn(C_{20}H_{20}N_2O_6S_2)]$ $[Bu_2Sn\ (C_2H_2OR)_2]$	Antimicrobial Antitumor & Anticancer	In vitro screening method. By the serial plate dilution method, spectroscopic techniques.	A.G. Hadi et al. [42]
9.	$[(Me)_2Sn$(2-benzoylpyridine N(4)-phenylthiosemicarbazone)$(CH_3COO).CH_3CH_2OH$ [(Ph)2Sn(2-benzoylpyridine N(4)-phenylthiosemicarbazone)(CH3COO)]CH3CH2OH [(Me)2Sn(2-acetylpyrazine N(4) phenylthiosemicarbazone)Cl [(Ph)2Sn(2-acetylpyrazine N(4) phenylthiosemicarbazone)(CH3COO)]	Antibacterial Antimicrobial	in vitro against selected bacteria and K562leukaemia cells	L.-Z. Zhang et al. [43]

Generally organotin compounds may bind with membrane proteins glycoprotein cellular proteins (eg. The hexokinase, ATPase, acetyl cholinesterase of the human erythrocyte membrane), and skeletal muscle membranes. They may also directly interact with DNA to cause cell death by either apoptotic or necrotic mechanisms. The tin compounds interact with the cell membrane or cell constituents in various ways. Thus the DNA is selected here as the potential target for antitumor activity studies. Because the three tin (IV) complexes 1-3 are isostructural the complex 1 was selected as a representative for the investigations of DNA binding and the comparison with the free H-ClQ ligand, the DNA binding properties of complex 1. From the above explanation it is clear, most of the tin complexes are very active against biological activity because the reactivity often complexes are very fast against bacteria and fungi due to strong coordination between metal and ligands. Investigation for some tin(IV)-fused azobenzene (TAz)complexes, are reported of the TAz complexes showed deep-red emission owing to the hypervalent bond composed of an electron-donating three-center four-electron (3c–4e) bond and an electron-accepting nitrogen–tin (N–Sn) coordination number from five to six. In photoluminescence (PL) spectra, the bands of these complex was the syntheses of the TAz complexes with hydrogens (TAz-H), halogens (TAz-F), electron-withdrawing groups (TAz-CF3) and electron-donating groups (TAz-Obu) that for the π-conjugation effects in relation to delocalization of the lone-pair electrons of fluorine or oxygen atoms seem to be positive for enhancing emission [34].

Tariq et al. in 2019 [44] designed triphenyltin(IV) complexes of 2–(4–ethoxybenzylidene) butanoate and exhibited greater antimicrobial and antitumor activities, A new organotin carboxylate based on 1,2,4,5-benzenetetracarboxylic acid H4L)[(Ph3Sn)4L] enhances fat solubility and plays an important role for the transportation of the organotin (IV) moiety to an active site cell membrane. In the field of heterocyclic chemistry for the π-conjugation systems such as the 1,2,4-triazole and other derivatives such as di- and tri-n-butyltin(IV) complexes of 2-{[5-(2-nitrophenyl) furan-2-yl]methyleneamino} benzoic acid have been reported to exhibit greater biocidal

activity as compared to methyltin (IV) specifically, tri-n-butyltin complex exhibited highest activity against Aspergillus parasiticus and Candida albicans with very low minimum inhibitory concentration (MIC) value. Another bioactivity of some few diphenyltin(IV) complexes of Schiff bases of the type Ph2SnL1-3 (L1: N-phenacyl-5-bromosalicylideneimine; L2:N-phenacyl-3,5-dichlorosalicylideneimine; L3N-phenacyl -4-methoxysalicylideneimine) were reported to exhibit mild antifungal activity against some fungi. $R_2Sn(IV)$ moiety, apart from the presence of the 1, antifungal activity results of complexes 1 and 2 indicate that the biological activity of HL exhibited a marked enhancement against the chosen fungal strains upon coordination with the organotin(IV) moiety, probably due to the presence of an azomethine (&labond; C═N─) linkage and/or the 2,4-triazole ring. By employing transition metal ions, dialkyltin(1V) dichloride, and glyoxal or biacetyl as templates, it has been possible to create binuclear macrocyclic complexes of L1–L4 in methanol. With the exception of other transition metal compounds like zinc (II), which are moisture sensitive and disintegrate slowly when exposed to air, all complexes are stable at ambient temperature for unlimited lengths of time. [53]

3. Conclusion

The majority of tin complexes are employed in biological processes. Tin compounds are frequently found in pharmaceuticals because they exhibit therapeutic properties. Tin complexes play a crucial role in medicine and exhibit minimal toxicity. The complexes produced by tin have a stronger affinity for interacting with ligands and are used in the medical industry. Three tin complexes 1-3, for instance, bind to ligands that are substituted with 5,7-dihalo-8-quinolines. BEL7404, SKOV-3, NCI-H460, and HL-7702 are used to test the cytotoxicity. The complexes exhibit strong anti-proliferative properties, with IC50 values between 20 nM and 5.11 M. Except in the cases of SKOV-3 and NCI-H460, complex 2. More so than quinolinol ligand, the whole complex strongly binds with DNA. That the result in literature often complexes are more useful in medicinal field but still more research works should be done in futures specially on chelating tin complexes.

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