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Synthesis, structural characterization and antibacterial activity of diorganotin(IV) complexes with ONO tridentate Schiff bases containing pyridine ring

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Abstract

Five organotin(IV) complexes, were obtained by reaction of SnR_2Cl_2 (R = Ph, Me, Bu) with ONO donor Schiff bases. The synthesized complexes have been investigated by elemental analysis and IR, ^1H NMR, and ^{119}Sn NMR spectroscopy. These data show that the Schiff base acts as a tridentate dianionic ligand and coordinates *via* the imine nitrogen and two oxygen atoms. The X-ray crystallography of complex **4** shows a dimeric structure for this molecule. 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 and compared with the standard antibacterial drugs.

Keywords: Schiff base; Antibacterial activity; Organotin(IV); Crystal structure; ^{119}Sn NMR

Schiff bases involving a pyridine ring have received considerable attention because of their very important role in biological systems. The organotin(IV) complexes of Schiff bases containing pyridine moiety have been tested on different microbial species and some of the complexes showed appreciable antimicrobial activities [1–3]. It has also been observed that a small structural change, such as the change of a substituent in the ligand may lead to enhanced biological activity of both free ligand and complex [4–7]. As part of our investigation on metal complexes of Schiff bases [8–11] and in order to investigate the role of organic group bound to tin and substituent in the ligand on biological activity, herein we have synthesized and studied structural and antibacterial properties of some diorganotin(IV) complexes with Schiff bases derived from 3-hydroxy-2-aminopyridine (Fig. 1).

2-((2-Hydroxynaphthalen-1-yl)methyleneamino)pyridin-3-ol (H_2L^a), 2-(2-hydroxy-3-methoxybenzylideneamino)-pyridin-3-ol (H_2L^b) and 2-(5-bromo-2-hydroxybenzylideneamino)pyridin-3-ol (H_2L^c) were prepared by refluxing a solution of 3-hydroxy-2-aminopyridine and corresponding aldehyde in 1:1 molar ratio in methanol for 1 h. $SnPh_2L^a$ (**1**), $SnPh_2L^b$ (**2**) and $SnPh_2L^c$ (**3**) $SnBu_2L^a$ (**4**) $SnMe_2L^a$ (**5**) have been synthesized by reaction of SnR_2Cl_2

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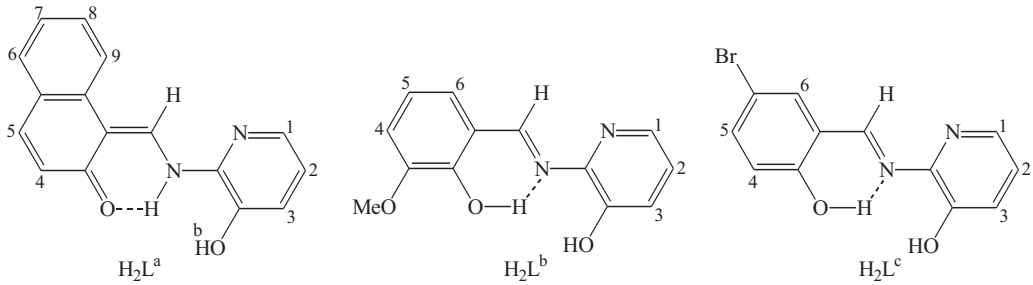

Fig. 1. Structure of Schiff base ligands.

(R = Ph, Bu and Me) with corresponding Schiff base in presence of NEt_3 in 1:1:2 molar ratio in methanol. **1**, **2** and **3** were obtained after stirring for 3 h, while **4** and **5** were refluxed for 5 and 3 h, respectively. The complexes $SnMe_2L^b$ (**6**) and $SnMe_2L^c$ (**7**) have been also prepared as literature [12,13] for antibacterial tests.

In the ^1H NMR spectra of H_2L^a the signal of CH=N and OH protons were appeared as doublet supporting the location of the hydrogen atom on the nitrogen atom and HCNH coupling. It indicates the keto-amine tautomeric form of H_2L^a is dominating in solution; while H_2L^b and H_2L^c are in phenol–imine form [12]. In the ^1H NMR spectra of the complexes, the complete absence of the signals due to the phenolic protons suggests deprotonation of ligands and coordination of corresponding anionic groups to tin. In the ^1H NMR spectra of complexes appearance of satellites around azomethine proton signal due to $^3J(^{119}Sn–^1H)$ coupling indicates the ligation of azomethine nitrogen to tin. The ^1H NMR spectrum of $SnMe_2L^a$ shows a singlet at low frequency (0.86 ppm) for $SnMe_2$ protons accompanied by satellites with $^2J(^{119}Sn–^1H)$ larger than uncomplexed $SnMe_2Cl_2$ (68.7 Hz) indicates the higher coordination number of tin [14]. Substitution of $^2J(^{119}Sn–^1H)$ in the Lockhart–Manders equation [15], gives a value of 129.2° for Me–Sn–Me angle in **5**. The $^{119}Sn\{^1H\}$NMR spectra of **1**–**5** show one sharp singlet significantly at −422.0, −433.7, −444.4, −235.9 and −153.6 ppm, respectively. These chemical shifts are at lower frequency than that of the original $SnPh_2Cl_2$ (−32 ppm), $SnBu_2Cl_2$ (122 ppm) and $SnMe_2Cl_2$ (+137 ppm) [14]. On the basis of the chemical shift ranges proposed empirically for organotin(IV) derivatives [16–18], the coordination number of tin is five for **5** in noncoordinating solvent ($CDCl_3$). However the ^{119}Sn signal for **1**–**4** in coordinating solvent (DMSO) lies at lower frequency than that for five-coordinated complexes of phenyltin and butyltin derivatives, since the solvent molecules coordinate to tin, shifting the signal to the region corresponding to hexacoordinated species [19] or it may be because of a dimeric structure retains in solution. In the IR spectra of all complexes the azomethine C=N band which appears at 1617–1625 cm^{-1} in free ligands, considerably shifts to the lower wavenumber (1591–1602 cm^{-1}) because the imine nitrogen is involved in coordination to the tin atom. The appearance of new bands in the IR spectra of the synthesized complexes in the region 443–449 and 513–548 cm^{-1}, which may be assigned to ν(Sn–N) and ν(Sn–O), respectively, supports the bonding of nitrogen and oxygen to the tin [5,9,20]. Presence of both ν_{sym}(Sn–C) and ν_{asym}(Sn–C) at 517 and 572 cm^{-1}, respectively, in the IR spectrum of **5** is consistent with a nonlinear Me–Sn–Me configuration.

The X-ray diffraction measurements for **4** were made on a STOE IPDS-IIT diffractometer with graphite monochromated Mo-Kα radiation. Cell constants and an orientation matrix for data collection were obtained by least-squares refinement of the diffraction data from 5839 unique reflections. Data were collected at a temperature of 120(2) K to a maximum 2θ value of 58.30°. The numerical absorption coefficients, μ, for Mo-Kα radiation are 1.198 mm^{-1}. Fig. 2 shows the molecular structure of $SnBu_2L^a$. This complex was crystallized in the monoclinic unit cell contains two molecules. The Schiff base behaves as tridentate dibasic ligand *via* imine nitrogen and two oxygen atoms. The geometry around the tin atom is distorted octahedral. The O, N, O-tridentate ligand is in a *mer* orientation to the tin octahedron. The two *n*-butyl substitutents are *trans* to each other, allowing the intermolecular coordination of the O2 with another tin to build a dimeric species. The Sn···O2 bond distance (2.729 Å) is longer than the sum of the covalent radii of the tin and oxygen (2.10 Å), but significantly shorter than the sum of the van der Waal's radii of these atoms (3.68 Å). The dimeric assembly occurs *via* the formation of a Sn_2O_2 four-membered ring. The Sn–O···Sn–O torsion angle is zero and show evidence of coplanarity. Therefore the tin environment is six coordinate and the pyridine atom has no participation in coordination to tin. The coordination part of ligand forms six and five membered chelate rings. These chelate rings are nearly planar as the torsion angles are small, Sn–O1–C1–C10 (−10.3°), Sn–O2–C13–C12 (4.0°), Sn–N1–C11–C10 (−6.6°) and Sn–N1–C12–C13 (−2.8°). The O···Sn bonding occurs with the oxygen atom at

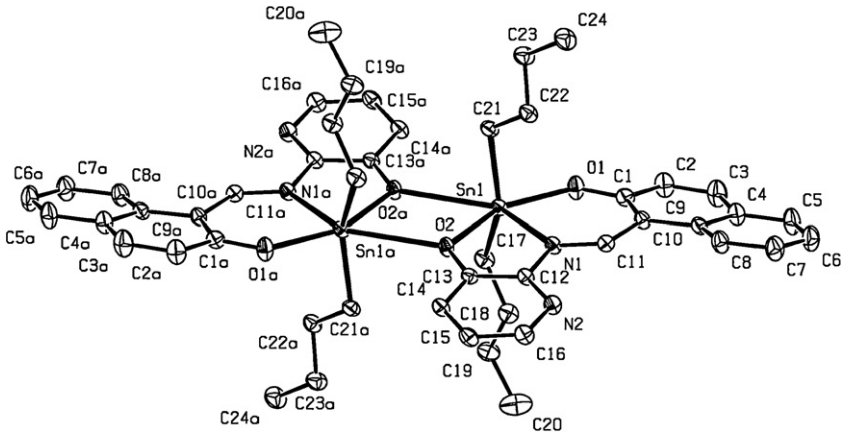

Fig. 2. ORTEP diagram of $SnBu_2L^a$.

the five-membered ring. The Sn–N1, Sn–O1 and Sn–O2 bond lengths are 2.187(2), 2.174(2) and 2.132(2) Å, respectively, which are very similar to the sum of the covalent radii of Sn–N (2.15 Å) and Sn–O (2.10 Å), indicating strong tin-nitrogen and tin-oxygen interactions.

The *in vitro* antibacterial activity of compounds was investigated against the standard strains of two Gram-positive (*Bacillus subtilis* ATCC 12711 and *Staphylococcus aureus* ATCC 6538) and two Gram-negative (*Escherichia coli* ATCC 11303 and *Pseudomonas aeruginosa* ATCC 27853) bacteria by paper-disc diffusion method. The compounds were dissolved in DMSO at 50 mg/mL concentration. Vancomycin (30 mg/disc), colistin (2 mg/disc), nalidixic acid (30 mg/disc) and erythromycin (15 mg/disc) were used as standard antibacterial drugs. Comparing the biological activity of the Schiff bases, organotin(IV) complexes and standard drugs (Table 1), indicate that H_2L^c has remarkable activity towards all bacterial strains. In general the activity of Schiff bases has been related to NH/OH groups which can play an important role in the antibacterial activity *via* hydrogen bonding with active sites of enzymes, also the imine group may impart in elucidating the mechanism of transformation reaction in biological system [21]. Remarkable activity of H_2L^c may also be related to presence of bromine in the structure of it. This finding agrees with previous report that the compounds having halogens at different positions of the aromatic ring showed a good inhibitory effect while compounds containing methoxy groups showed less inhibition on microbial growth [22]. The results show that complexes **2** and **6** exhibit more inhibitory effects than the parent ligand against *B. subtilis, S. aureus* and *P. aeruginosa*. In general, enhancement in activity of complexes may be due to the increasing of lipophilic character and efficient diffusion of the metal complexes into bacterial cell upon the coordination of ligand to metal (chelation theory) [23–26] and also because of the intrinsic biological activity effects of organotin moiety. It is interesting that *P. aeruginosa* was well inhibited by **6**, while standard drugs were found to have no activity against it.

On the basis of above discussion, Schiff bases are completely deprotonated and coordinated to the tin through imine nitrogen and two oxygen atoms, and the pyridine nitrogen atom has no participation in the coordination to the tin. The synthesized organotin complexes show different activities against studied bacterial species and the Schiff base with bromine on aromatic ring (H_2L^c) exhibits the most inhibitory effect.

Table 1
Antibacterial activity data of ligands and their organotin(IV) complexes.

Microorganism	Inhibition zone (mm)													
	H_2L^a	H_2L^b	H_2L^c	**1**	**2**	**3**	**4**	**5**	**6**	**7**	V	C	N	E
E. Coli	n.a	21	47	n.a.	12	12	10	9	15	n.a.	18	12	28	20
P. aeruginosa	10	16	15	n.a.	8	17	n.a.	n.a.	20	10	n.a.	n.a.	n.a.	n.a.
S. aureus	n.a.	16	40	10	27	22	12	10	17	11	18	28	16	28
B. subtilis	9	15	38	n.a.	20	20	n.a.	n.a.	17	11	24	30	28	30

n.a., no activity; V, vancomycin; C, clistin; N, nalidixic acid; E, erythromycin.

Supplementary data

CCDC 859451 contains the supplementary crystallographic data for **4**. These data can be obtained free of charge via http://www.ccdc.cam.ac.uk/conts/retrieving.html.

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