

# Template Synthesis of Sn(II), Sn(IV) and Co(II) complexes *via* 3-Aminopropyltriethoxysilane and Salicylaldehyde and Evaluate their Antibacterial Sensitivity

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Template method reaction of  $SnCl_2 \cdot 2H_2O$  or  $SnCl_4 \cdot 5H_2O$  or  $CoCl_2 \cdot 6H_2O$  with 3-aminopropyltriethoxysilane and salicyaldehyde have been carried out to prepare three metal complexes;  $C_{32}H_{53}N_2O_8ClSnSi_2(\mathbf{A})$ ,  $C_{32}H_{53}N_2O_8Cl_3SnSi_2(\mathbf{B})$  and  $C_{32}H_{52}N_2O_8CoSi_2(\mathbf{C})$ . The prepared metal complexes were characterized by analytical techniques *viz.*, FT-IR, <sup>1</sup>H NMR, UV-visible, CHNS elemental and molar conductivity. The analytical data shows that the metal ion to ligand (Schiff base) ratio in the prepared complexes was in 1:2. Octahedral structures were proposed for **A** and **B** complexes while **C** complex has a tetrahedral structure. The antibacterial activity of metal complexes were investigated against *Streptococcus pneumoniae* (Gram-negative) and *Proteus* (Gram-positive). The results showed that all the prepared complexes diminished the bacterial growth.

Keywords: Template method, 3-Aminopropyltriethoxysilane, Tin, Cobalt, Complexes, Octahedral structure, Antibacterial sensitivity.

# **INTRODUCTION**

In template method, a metal ion can play an important role in directing the reaction towards the desired ligand product, or aiding its isolation. Example for template method is the reaction between ethylene diamine and 2,5-dihydroxyacetophenone in the presence of acetate uranyl solution [1-6]. When the change of amines or aldehydes can be obtained an assortment of Schiff bases. Thus synthesis of large number of Schiff bases with different structural features could be possible with ease. They can have additional donor atoms like phosphorus, oxygen, sulphur, etc. which makes them good donor atoms for metal ion complexation and for mimicking biological systems. They can be functionalized by the insertion of appropriate groups in the aliphatic or aromatic chains [7]. Template method has been used to prepare compounds that have remarkable topologies, such as helicates, rotaxanes and catenanes [8]. Schiff base complexes of Mn(II), Fe(III), Co(II), Ni(II), Cu(II) and Zn(II) have been prepared via template method using L-histidine, guinoxaline-2-carboxyaldehde and metal ion [9]. As well as template method used to prepare complexes

derived from the macrocyclic ligands in the presence of CrCl<sub>3</sub>·6H<sub>2</sub>O. The ligands and their complexes have been characterized in different physical techniques and evaluated for their pesticidal, nematicidal and antimicrobial activities [10]. Nickel(II) complexes of substituted dibenzotetraaza-[14]annulenes have been synthesized by template reactions starting from either 1,2-diamines with  $\beta$ -diketones or 1,5-benzodiazepinium salts in the presence of Ni(II) contain symmetrical macrocycles [11]. The complexes of Cr(III), Mn(III) and Fe(III) have been prepared by template condensation of oxalyldihydrazide and benzil in methanolic medium forming metal complexes of type  $[M(C_{32}H_{24}N_8O_4)X]X_2$  where M = Cr(III), Mn(III), Fe(III) and  $X = Cl^{-}$ ,  $NO_{3}^{-}$ ,  $CH_{3}COO^{-}$ . The complexes have been characterized by elemental analyses, molar conductivity, magnetic susceptibility measurements and spectral studies such as UV-visible, NMR, FT-IR, etc. On the basis of these studies, a five coordinate square pyramidal geometry has been proposed for all these complexes, biological activities of the metal complexes have been tested in vitro against a number of pathogenic bacteria to evaluated their inhibiting potentiality [12]. Murphy et al. [13] prepared cobalt and copper complexes

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by template method through mixing metal acetate (1 mol) and salicyaldehyde (2 mol) and 3-aminopropyltriethoxysilane (2 mol) using acetonitrile as solvent. In this paper, we reported the synthesis Co(II), Sn(II) and Sn(IV) complexes by template reaction *via* 3-aminopropyltriethoxysilane and salicyaldehyde with metal chlorides by using absolute ethanol as solvent.

## **EXPERIMENTAL**

All the solvents and chemicals were supplied by (Sigma-Aldrich) and used without purification. Elemental analysis (CHNS) of complexes was estimated using (EuroEA Elemental Analyzer). The molar conductance of complexes was measured by preparing  $10^{-3}$  M solutions in DMSO solvent using Digital conductivity Meter-WT-700-inolab at room temperature. UVvisible spectra were recorded in DMSO on a Shimadzu UV-1800 spectrophotometer. FT-IR spectra of the complexes were recorded using KBr pellets in Shimadzu spectrophotometer in the region of 4000-400 cm<sup>-1</sup>. Magnetic susceptibility were measured for complexes by Auto magnetic susceptibility balance Sherwood Scientific. The proton nuclear magnetic resonance (<sup>1</sup>H NMR) spectra were recorded in DMSO- $d_6$  solution using tetramethylsilane (TMS) as the internal standard in 400 MHz NMR spectrophotometer.

Synthesis of the metal complexes: The new tin cobalt complexes were synthesized using template method by condensing 3-amino-propyltriethoxysilane and salicyaldehyde in the presence of the respective metal salt. To a hot stirring ethanolic solution 10 mL of 3-aminopropyltriethoxysilane (2 mol, 0.5 g) and 0.5 mL of salicyaldehyde (2 mol, 0.2 g) was added CoCl<sub>2</sub>·6H<sub>2</sub>O or SnCl<sub>2</sub>·2H<sub>2</sub>O or SnCl<sub>4</sub>·5H<sub>2</sub>O (1 mol) dissolved in the minimum quantity of ethanol (5 mL). The resulting solution was heated under reflux for 2 h. The final product was filtered and washed with cold methanol several times and lastly dried at 45 °C for 24 h.

 $\begin{array}{c} \textbf{C}_{32}\textbf{H}_{53}\textbf{N}_2\textbf{O}_8\textbf{ClSnSi}_2 \ \textbf{complex:} \ \textbf{m.p.:} \ 313 \ ^\circ \textbf{C}. \ decomp.\\ Molar \ conductivity (\mu S/cm) \ is \ 63 \ ohm^{-1} \ cm^2 \ mol^{-1}. \ FT-IR \ (KBr, \nu_{max}, \ cm^{-1}): \ 3406 \ (br), \ 3140 \ (w), \ 2972 \ (w), \ 2929 \ (w), \ 1739 \ (w), \ 1660 \ (s), \ 1620 \ (s), \ 1550 \ (s), \ 1475 \ (s), \ 1410 \ (w), \ 1355 \ (w), \ 1276 \ (m), \ 1207 \ (m), \ 1155 \ (s), \ 1037 \ (s), \ 904 \ (w), \ 761 \ (s), \ 692 \ (w), \ 470 \ (w), \ 455 \ (m). \ Elemental \ anal. \ calcd. \ (\%): \ C, \ 47.80; \ H, \ 6.64; \ N, \ 3.48; \ Found: \ C, \ 48.29; \ H, \ 6.47; \ N, \ 3.99. \end{array}$ 

 $\begin{array}{l} \textbf{C}_{32}\textbf{H}_{53}\textbf{N}_2\textbf{O}_8\textbf{C}l_3\textbf{SnSi}_2 \ \textbf{complex:} \text{ m.p.: } 307 \ ^\circ \textbf{C}. \ decomp. \ Molar \ conductivity (\mu S/cm) \ is 40 \ ohm^{-1} \ cm^2 \ mol^{-1}. \ FT-IR \ (KBr, \nu_{max}, \ cm^{-1}): \ 3350 \ (br), \ 3059 \ (w), \ 1646 \ (m), \ 1602 \ (s), \ 1543 \ (s), \ 1479 \ (s), \ 1460 \ (s), \ 1439 \ (s), \ 1382 \ (m), \ 1319 \ (s), \ 1179 \ (s), \ 1130 \ (w), \ 1100 \ (s), \ 951 \ (m), \ 838 \ (m), \ 771 \ (m), \ 756 \ (m), \ 694 \ (s), \ 656 \ (m), \ 505 \ (m). \ Elemental \ anal. \ calcd. \ (\%): \ C, \ 43.92; \ H \ 6.11; \ N \ 3.20; \ Found: \ C, \ 44.23; \ H, \ 6.53; \ N, \ 3.78. \end{array}$ 

 $\begin{array}{l} \textbf{C}_{32}\textbf{H}_{52}\textbf{N}_2\textbf{O}_8\textbf{CoSi}_2 \ \textbf{complex:} \ \textbf{m.p.:} 288 \ ^\circ \textbf{C}. \ decomp. \ Molar \\ \textbf{conductivity} \ (\mu S/cm) \ is \ 22 \ ohm^{-1} \ cm^2 \ mol^{-1}. \ FT-IR \ (KBr, \nu_{max}, \\ cm^{-1}): \ 3433 \ (br), \ 3180 \ (br), \ 2931 \ (w), \ 2360 \ (s), \ 1712 \ (w), \ 1658 \\ (s), \ 1606 \ (s), \ 1552 \ (s), \ 1479 \ (s), \ 1411 \ (w), \ 1274 \ (m), \ 1297 \\ (m), \ 1091 \ (w), \ 900 \ (m), \ 763 \ (m), \ 698 \ (w), \ 588 \ (w), \ 503 \ (w). \\ Elemental \ anal. \ calcd. \ (\%): \ C, \ 54.30; \ H \ 7.40; \ N \ 3.96; \ Found: \\ \textbf{C}, \ 54.54; \ H, \ 7.76; \ N, \ 3.56. \end{array}$ 

#### **RESULTS AND DISCUSSION**

**IR analysis:** FT-IR spectra of the complexes have been studied in order to characterize their structures. In Figs. 1-3,

the characteristic FT-IR spectra of the prepared metal complexes are shown. In tin complexes (A and B), the bands around (3450-3420 cm<sup>-1</sup>) can be exhibited for hydroxyl group in complexes [14]. The band between 3200-2900 cm<sup>-1</sup> for C-H aromatic and C-H aliphatic, respectively. According to literature [15,16], azomethine group (-CH=N-) in free ligand (salicylaldehyde with 3-aminopropyltriethyoxysilane) at 1632 cm<sup>-1</sup>, while in tin complexes, it appeared between 1660-1658 cm<sup>-1</sup> and cobalt complex at 1618 cm<sup>-1</sup> due to the coordination of metal ion with nitrogen of azomethine group (-CH=N-). Other important stretches are v(C=C) of aromatic ring observed between 1479 - 1460 cm<sup>-1</sup>, as well as  $\nu$ (C-O) where C-O is attached to aromatic ring, which is found between 1279-1276 cm<sup>-1</sup> [15]. The bands around 1280-1200 cm<sup>-1</sup> v(C-O) for ethoxy group. The bands at 1091-1051 cm<sup>-1</sup> are due to the vibration of Si-O bands in both ligands and complexes. The bands around 760-686 and 686-500 cm<sup>-1</sup> may be attributed to (M-N) and (M-O) stretching, respectively [17].



**Electronic spectra:** The electronic spectra of prepared complexes were measured in DMSO solvent in  $1 \times 10^{-3}$  M at room temperature. The UV-visible spectra for tin complexes pointed two absorption bands between 206-327 nm. These absorption bands are assigned to both Schiff base transition  $(\pi-\pi^*, n-\pi^*)$  and charge transfer transition from the metal to antibonding orbital of Schiff base and these transition is high intensity due to no subject selection rules [18]. In Fig. 4, UV-visible spectrum of cobalt complex (C) has showed four absorption bands at 206 and 325 nm for  $(\pi-\pi^*, n-\pi^*)$ , respectively while band at 400-700 nm in cobalt complex belong to *d-d* transition in tetrahedral complexes [19].



Fig. 4. UV-visible spectrum for C complex

**Conductance measurements:** The observed molar conductances in  $10^{-3}$  M DMSO solutions for tin complexes were 40-63 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, which indicated that conductivity is 1:1, while for cobalt complex in  $10^{-3}$  M DMSO solution is 22 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup> [20].

**Magnetic moments:** The magnetic moment value for **A** and **B** complexes were found to be 0.0 B.M., thus confirming diamagnetic nature and have octahedral structures. While magnetic moment value for complex **C** was 4.4 B.M., which showed a paramagnetic nature and had tetrahedral shape because there are lone electrons which had configuration  $e^4t_2^3$  [6].

<sup>1</sup>H NMR analysis: <sup>1</sup>H NMR spectra of complexes showed an expected resonances for propyltriethoxysilane (0.57-4 ppm) and aromatic ring (6.6 - 7.6 ppm) regions, while the protons of azomethine group (8.5-9.5 ppm). The <sup>1</sup>H NMR spectra of tin complexes (**A** and **B**) show the hydroxyl protons appeared between  $\delta$  10.24-10.73 ppm.

The protons of methylene group  $(SiCH_2CH_2CH_2)$  on the propyl group in all complexes appeared between  $\delta$  1.00-0.58 ppm. The methyl protons ( $CH_3CH_2OSi$ ) in the methoxy group appeared between  $\delta$  1.47-1.71 ppm. The protons of methylene group (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) on propyl group in all complexes appeared between  $\delta$  2.00-2.49 ppm. While the protons of methylene group (SiCH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>CH<sub>2</sub>) appeared between  $\delta$  2.49-2.77 ppm near to azomethine group. The protons of methylene group (CH<sub>3</sub>CH<sub>2</sub>-OSi) in methoxy group appeared between  $\delta$  3.34-3.47 ppm. The methylene protons resonate more downfield than methyl protons due to close proximity of oxygen atom. In free ligand, the chemical shift of hydrogen for hydroxyl (-OH) and imine group -CH=N-found as a singlet at  $\delta$  13.6 and  $\delta$  8.35 ppm, respectively [15]. While in synthesized complexes, the chemical shift of hydroxyl group found at ( $\delta$  10.24-10.73 ppm) and imine group at (8.5-9.5 ppm), this changes is due to the coordination of oxygen and nitrogen with metal ion [14,15]. The complete <sup>1</sup>H NMR spectral data for synthesized complexes are shown in Table-1.

**Proposed structure of complexes:** From the results of CHN elemental analysis, UV-visible, magnetic susceptibility, molar conductivity and <sup>1</sup>H NMR spectra of complexes, the proposed structure of these compounds were octahedral geometry for tin complexes and tetrahedral geometry for cobalt complex (Fig. 5).

**Antibacterial activity:** Antibacterial activity of synthesized complexes **A**, **B** and **C** were tested by agar-well diffusion techniques as described by Agarry *et al.* [21]. The wells of 6 mm diameter were cut on sterile nutrient agar plates and swabbed with nutrient broth. Bacterial species were collected from Department of Biology, Mycology Lab., College of Science. The test bacteria used for assay are *Streptococcus pneumoniae* (Gram-negative) and *Proteus* (Gram-positive). Each well was loaded 0.25 mL the solution of each complex with concentration (10<sup>-3</sup> M in DMSO as solvent) and placed on the already seeded plates and incubated at 37 °C. Antibacterial activity of these complexes evaluated by measuring inhibition zone (IZ)

TABLE-1 <sup>1</sup> H NMR SPECTRAL DATA (δ ppm) OF A, B AND C COMPLEXES							
Complex	$SiCH_2CH_2CH_2$	CH <sub>3</sub> CH <sub>2</sub> OSi	$SiCH_2CH_2CH_2$	$SiCH_2CH_2C\underline{H}_2$	$CH_3C\underline{H}_2OSi$	-N=C <u>H</u>	Ar-O <u>H</u>
А	0.60	1.71	2.49	2.76	3.34	8.81	10.24, 10.72
В	0.57	1.68	2.48	2.77	3.35	8.58	10.24, 10.73
С	1.03	1.42	2.05	2.49	3.47	9.51	-



Fig. 5. Proposed structures of the A, B and C complexes

TABLE-2 INHIBITION ZONE OF COMPLEXES SYNTHESIZED AGAINST PATHOGENIC BACTERIA							
Complexes	Inhibition zone (mm) of bacteria						
	Streptococcus pneumoniae	Control AK	Solvent DMSO	Proteus	Control AK	Solvent DMSO	
Α	16	17	0	20	19	0	
В	17	17	0	17	19	0	
С	15	17	0	15	19	0	
L.S.D.	N.S			2.288			

after 24 h of incubation. Complexes were tested against test bacteria in triplicates. Amikacin antibiotic was used as control. The discs were then turned upside down and incubated at 37°C for 24 h. Table-2 showed the results of antibacterial activity of complexes solution in concentration  $(1 \times 10^{-3} \text{ M})$  measured in mm. The inhibition zones for antibiotic (amikacin) in streptococcus and proteins were fund to be as 17 and 19 mm, respectively. The results showed that all synthesized complexes diminished the bacterial growth. The inhibition zone for compounds A and C in *Streptococcus pneumoniae* are less than from antibiotic (amikacin). While the inhibition zone for compound A in proteins is larger than amikacin. The inhibition zones recorded for compounds **B** and **C** in proteins bacteria were 15 and 16 mm, respectively. These activities for metal complexes with both pathogenic bacteria may be explained by polarity concept [22], where the chelation minimize the polarity of metal atom mainly because of the partial sharing of its positive charge in Schiff base, which favors permeation of the synthesized metal complexes through the lipid layer of cell membrane. The mode of action of metal complexes may involve hydrogen bonding via nitrogen azomethine group with active centers of cell ingredients resulting in the interference with normal cell operation. Furthermore, the content of these compounds from oxygen atom which may be bind with enzyme leading inactivating some of the enzymes [23].

## Conclusion

The spectral studies indicated that the Schiff base formed from template reaction with metal ion behaves as a bidentate ligand through (O,N) atoms. From the elemental analysis, magnetic studies, conductance measurements and various spectral studies it is concluded that the metal:ligand stoichiometric ratio is 1:2 in all the complexes. *in vitro* Antibacterial studies of these complexes are effective against *Streptococcus pneumoniae* (Gram-negative) and *Proteus* (Gram-positive).

# **CONFLICT OF INTEREST**

The authors declare that there is no conflict of interests regarding the publication of this article.

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