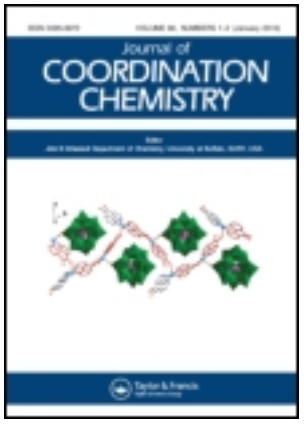

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Dimeric and monomeric six-coordinate tin(IV) complexes: synthesis and spectral (IR, NMR (^{1}H, ^{13}C, ^{119}Sn), TOF-MS, and ESI-MS) studies

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Dimeric and monomeric six-coordinate tin(IV) complexes: synthesis and spectral (IR, NMR (^{1}H, ^{13}C, ^{119}Sn), TOF-MS, and ESI-MS) studies

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Six-coordinate dimeric tin(IV) complexes, $[(\mu\text{-Cl})_2Sn_2(\eta^2\text{-sb})_2Cl_4]$ {where sb = salicylidene-2-methyl-1-aminobenzene (o-smab**H**) (**1**), salicylidene-4-methyl-1-aminobenzene (p-smab**H**) (**2**), and salicylidene-2-aminopyridine (sap**H**) (**3**)}, have been synthesized by interactions of tin(IV) chloride with the appropriate sodium salt of Schiff bases in 1 : 1 M ratio in isopropanol-benzene. These complexes have been characterized by elemental (C, H, N, and Sn) and spectral [IR, NMR (^{1}H, ^{13}C, ^{119}Sn), TOF-MS, and ESI-MS] studies. Complexes **1**–**3** on treatment with an excess of THF afford mononuclear six-coordinate tin(IV) complexes, $[(sb)SnCl_3\cdot THF]$, **4**–**6**. The biological activities (*e.g.* antimicrobial action) of the synthesized Schiff bases and **1**–**3** were assessed by *in vitro* testing on the growth of various strains of bacteria and fungi.

Keywords: Synthesis; Sn(IV) complexes; IR; NMR; MS spectra

1. Introduction

The chemistry of tetravalent metal(loid) complexes derived from N-arylsalicylaldimine ligands [1, 2] remains of interest from synthetic, physicochemical, and structural points of view. Our research group has been involved for synthesis and characterization of new chloro-bridged dimeric and monomeric complexes of Schiff bases with different metals [3–8]. No such chloro-bridged $[Sn(\mu\text{-Cl})_2Sn]$ complexes of tin(IV) have been reported [9–11]. The present investigation assumes additional importance due to established toxicological, biochemical, agricultural, and industrial applications [12–16] of tin(IV) compounds. As part of our continued interest in tin(IV) and organotin(IV) complexes derived from Schiff base ligands [17–20], we describe herein the synthesis and spectral [IR (^{1}H, ^{13}C, ^{119}Sn) NMR, TOF-MS, and ESI-MS] studies of dimeric $[(\mu\text{-Cl})_2Sn_2(\eta^2\text{-sb})_2Cl_4]$ (**1**–**3**) and monomeric $[(sb)SnCl_3\cdot THF]$ (**4**–**6**) complexes of tin(IV).

2. Experimental

All chemicals and reagents used were of analytical grade. Tin tetrachloride was distilled prior to use. Salicylaldehyde (Loba), 2-aminopyridine (Merck), o-toludine (BDH), and p-

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toludine (Merck) were purified by distillation. Solvents were dried prior to use according to literature procedures [21]. Elemental (C, H and N) analyses were performed on a Haraeus Carlo Erba 1108 elemental analyzer. Tin was estimated gravimetrically as SnO_2 after decomposition of complexes with concentrated HNO_3. Chlorine was estimated volumetrically by using the Volhard method [22]. Infrared spectra (4000–400 cm^{-1}) were recorded on a Perkin Elmer 100 FT-IR spectrophotometer and Nicole Instrument MAGMA 550 was used to record spectra from 600 to 50 cm^{-1}. NMR (^1H, ^{13}C, and ^{119}Sn) spectra were recorded in a mixture of DMSO-d_6 and $CDCl_3$ on a Bruker DRX-300 spectrometer. Chemical shifts are given in ppm relative to Me_4Si (^1H, ^{13}C) and Me_4Sn (^{119}Sn). Mass spectra were recorded on WATERS TOF MS/MS and Agilent 6520 Q-Tof LCMS, MS/MS spectrometers.

2.1. *Syntheses*

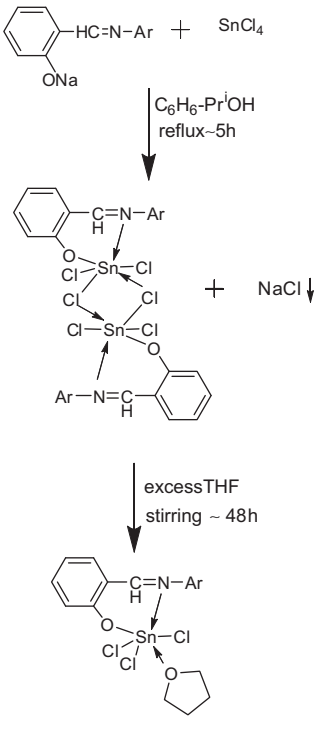
2.1.1. Synthesis of schiff bases. The Schiff bases were synthesized according to the procedure described in earlier publications [19, 20].

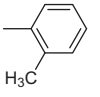
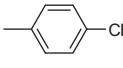
2.1.2. Synthesis of complexes. Similar procedure was used for preparation of **1**–**3**; for the sake of brevity, general preparative details (scheme 1) are given. To a benzene (20 mL) solution of $SnCl_4$, equimolar amount of an appropriate sodium salt of Schiff base [prepared by reaction of equimolar amounts of sodium metal and a Schiff base (**H**L) in isopropanol (30 mL)] was added dropwise with constant stirring. The reaction mixture was refluxed for 5 h and precipitated NaCl was removed by filtration. The solvent was removed by distillation. The solid products were dried under reduced pressure and recrystallized from THF-hexane.

2.1.2.1. [(μ-Cl)$_2$Sn$_2$(o-smab)$_2$Cl$_4$] **(1)**. Yield: 69%; dark yellow solid; m.p. 96–98 °C; Anal. Calcd for $C_{28}Cl_6H_{24}N_2O_2Sn_2$ (%): C, 38.3; H, 2.7; N, 3.2; Cl, 24.4; Sn, 27.2. Found: C, 38.0; H, 2.2; N, 2.9; Cl, 24.2; Sn, 26.2. IR (KBr pellets, cm^{-1}): 1598 ($\nu_{C=N}$), 1296(ν_{C-O}), 537(ν_{Sn-O}), 460($\nu_{Sn\leftarrow N}$), 324($\nu_{Sn-Cl\ terminal}$), 227($\nu_{Sn-Cl-Sn\ bridging}$). ^1H NMR ($CDCl_3$, δ_H): 8.52(2H, s, CH=N), 6.88–7.37(m, 16H, Ar-H), 2.32(6H, s, Ar-CH_3), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 161.92 (s, CO), 159.28 (s, CN), 116.68–138.41 (s, Ar-C), 17.75 (s, Ar-CH_3), ppm. ^{119}Sn NMR (DMSO-d_6, δ_{Sn}): -618.96, ppm. TOF-MS: Found 873.3894, Calcd 870.64.

2.1.2.2. [(μ-Cl)$_2$Sn$_2$(p-smab)$_2$Cl$_4$] **(2)**. Yield: 73%; yellow solid; m.p. 106–108 °C; Anal. Calcd for $C_{28}Cl_6H_{24}N_2O_2Sn_2$ (%): C, 38.3; H, 2.7; N, 3.2; Cl, 24.4; Sn, 27.2. Found: C, 38.1; H, 2.3; N, 2.9; Cl, 24.1; Sn, 26.6. IR (KBr pellets, cm^{-1}): 1607($\nu_{C=N}$), 1287 (ν_{C-O}), 543(ν_{Sn-O}), 454($\nu_{Sn\leftarrow N}$), 327($\nu_{Sn-Cl\ terminal}$), 230($\nu_{Sn-Cl-Sn\ bridging}$). ^1H NMR ($CDCl_3$, δ_H): 8.60(2H, s, CH=N), 6.58–7.89(m, 16H, Ar-H), 2.27(6H, s, Ar-CH_3), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 161.15 (s, CO), 159.46 (s, CN), 115.33–140.64 (s, Ar-C), 16.61 (s, Ar-CH_3), ppm. ^{119}Sn NMR (DMSO-d_6, δ_{Sn}): −621.87, ppm. ESI-MS: Found 875.1, Calcd 870.64.

2.1.2.3. [(μ-Cl)$_2$Sn$_2$(sap)$_2$Cl$_4$] **(3)**. Yield: 73%; dark brown solid; m.p. 126–127 °C; Anal. Calcd for $C_{24}Cl_6H_{18}N_4O_2Sn_2$ (%): C, 34.1; H, 2.1; Cl, 25.1; N, 6.6; Sn, 28.1. Found: C,



Complex	(**1**), (**4**)	(**2**), (**5**)	(**3**), (**6**)
Ar-			

Scheme 1. Synthesis of **1**–**6**.

33.9; H, 1.9; Cl, 24.8; N, 6.4; Sn, 26.4. IR (KBr pellets, cm^{-1}): 1612($\nu_{C=N}$), 1504 ($\nu_{C=N\ pyridine}$), 1286($\nu_{C\text{-}O}$), 542($\nu_{Sn\text{-}O}$), 440($\nu_{Sn\leftarrow N}$), 303($\nu_{Sn\text{-}Cl\ terminal}$), 228($\nu_{Sn\text{-}Cl\text{-}Sn\ bridging}$). ^{1}H NMR ($CDCl_3$, δ_H): 9.93(2H, s, CH=N), 6.65–8.44(m, 14H, Ar-H), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 163.81 (s, CO), 160.33 (s, CN), 117.90–148.00 (s, Ar-C, Py-C), ppm. ^{119}Sn NMR (DMSO-d_6, δ_{Sn}): −621.02, ppm. ESI-MS: Found 847.5, Calcd 844.57.

Mononuclear **4**–**6** were prepared by treating **1**–**3** with an excess of THF followed by stirring 48 h.

2.1.2.4. [(o-smab)$SnCl_3$·THF] (**4**). Yield: 83%; dirty green solid; m.p. 89–91 °C; Anal. Calcd for $C_{18}Cl_3H_{20}NO_2Sn$ (%): C, 42.6; H, 3.9; Cl, 20.9; N, 2.7; Sn, 23.3. Found: C, 42.3; H, 3.7; Cl, 20.4; N, 2.6; Sn, 22.9. IR (KBr pellets, cm^{-1}): 1602($\nu_{C=N}$), 1279($\nu_{C\text{-}O}$), 1076 ($\nu_{C\text{-}O\text{-}C\ THF}$), 539($\nu_{Sn\text{-}O}$), 445($\nu_{Sn\leftarrow N}$), 445($\nu_{Sn\leftarrow O\ THF}$), 328($\nu_{Sn\text{-}Cl\ terminal}$). ^{1}H NMR ($CDCl_3$, δ_H): 8.51(H, s, CH=N), 6.64–7.29(m, 8H, Ar-H), 3.15–3.55(m, 2H^a, THF), 2.28 (s, Ar-CH_3), 1.07–1.87(m, 2H^b, THF), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 163.81 (s, CO), 160.33 (s, CN), 117.90–148.00 (s, Ar-C), 66.93 (s, C^a-THF), 24.71 (s, C^b-THF), 17.35(s,

Ar-CH_3), ppm. ^{119}Sn NMR (DMSO-d_6, δ_{Sn}): -631.06, ppm. ESI-MS: Found 510.3, Calcd 507.4.

2.1.2.5. [(p-smab)$SnCl_3$·THF] (**5**). Yield: 88%; green solid; m.p. 87–88 °C; Anal. Calcd for $C_{18}Cl_3H_{20}NO_2Sn$ (%): C, 42.6; H, 3.9; Cl, 20.9; N, 2.7; Sn, 23.3. Found: C, 42.4; H, 3.8; Cl, 20.5; N, 2.5; Sn, 22.9. IR (KBr pellets, cm^{-1}): 1598($\nu_{C=N}$), 1284($\nu_{C\text{-}O}$), 1068 ($\nu_{C\text{-}O\text{-}C\ THF}$), 532($\nu_{Sn\text{-}O}$), 435($\nu_{Sn\leftarrow N}$), 440($\nu_{Sn\leftarrow O\ THF}$), 328($\nu_{Sn\text{-}Cl\ terminal}$). ^{1}H NMR ($CDCl_3$, δ_H): 8.32(H, s, CH=N), 6.40–7.97(m, 8H, Ar-H), 3.57–4.00(m, 2H^a, THF), 2.22(s, Ar-CH_3), 1.22–1.58(m, 2H^b, THF), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 161.81 (s, CO), 160.57 (s, CN), 116.67–138.32 (s, Ar-C), 68.01 (s, C^a-THF), 21.66 (s, Ar-CH_3), 27.28 (s, C^b-THF), ppm. ^{119}Sn NMR (DMSO-d_6, δ_{Sn}): −623.14, ppm. ESI-MS: Found 509.6, Calcd 507.4.

2.1.2.6. [(sap)$SnCl_3$·THF] (**6**). Yield: 78%; brown solid; m.p. 110–113 °C Anal. Calcd for $C_{16}Cl_3H_{17}N_2O_2Sn$ (%): C, 38.8; H, 3.4; Cl, 21.5; N, 5.6; Sn, 24.0. Found: C, 38.6; H, 3.2; Cl, 21.3; N, 5.2; Sn, 23.8. IR (KBr pellets, cm^{-1}): 1615($\nu_{C=N}$), 1500 ($\nu_{C=N\ pyridine}$), 1281($\nu_{C\text{-}O}$), 1058 ($\nu_{C\text{-}O\text{-}C\ THF}$), 536($\nu_{Sn\text{-}O}$), 443($\nu_{Sn\leftarrow N}$), 424($\nu_{Sn\leftarrow O\ THF}$), 301($\nu_{Sn\text{-}Cl\ terminal}$). ^{1}H NMR ($CDCl_3$, δ_H): 9.93(H, s, CH=N), 6.86–8.57(m, 7H, Ar-H, Py-H), 3.38–3.65(m, 2H^a, THF), 1.00–1.81(m, 2H^b, THF), ppm. ^{13}C NMR ($CDCl_3$, δ_C): 162.24 (s, CO), 158.90 (s, CN), 110.70–142.16(s, Ar-C, Py-C), 66.85 (s, C^a-THF), 26.40 (s, C^b-THF), ppm. ^{119}Sn NMR (DMSO-d_6, δ_{Sn}): −639.34, ppm. ESI-MS: Found 493.4, Calcd 494.39.

3. Results and discussion

Equimolar reactions of tin(IV) chloride with sodium salts of Schiff bases afford chloride-bridged **1**–**3**, which on treatment with an excess of THF followed by stirring for 48 h yield mononuclear **4**–**6** (scheme 1). All these complexes are yellow-brown solids, soluble in methanol, ethanol, isopropanol, chloroform, DMSO, or DMF.

3.1. *Infrared spectra*

Salient features of IR spectra are the disappearance of stretch due to phenolic (O–H) at 3484–3430 cm^{-1}, assigned to deprotonation of phenolic hydrogen on complexation [23]. Such interaction is also supported by shift of $\nu_{C\text{-}O}$ 16–24 cm^{-1} to higher frequency, with respect to parent Schiff bases. The appearance of new bands at 543–532 cm^{-1} are assignable [24] to $\nu_{Sn\text{-}O}$. Coordination through azomethine nitrogen was supported by shift of $\nu_{C=N}$ (1615–1598 cm^{-1}) to lower frequencies from 1634–1616 cm^{-1} in free Schiff bases [19, 20]. Coordination of azomethine nitrogen was further supported by a band at 460–440 cm^{-1} due to Sn←N stretch [25]. In **4**–**6** C–O–C stretches of coordinated THF were observed at 1076–1058 cm^{-1} consistent with coordination [26] of THF, further supported by mass and ^{119}Sn NMR studies. In **1**–**3** a band assignable to $\nu_{Sn\text{-}Cl}$ was observed at 230–227 cm^{-1}, characteristic of bridging chloride [27, 28] and supporting the dimeric nature of these complexes. Dimeric **1**–**3** and monomeric **4**–**6** are supported by mass and ^{119}Sn NMR spectral studies. The noninvolvement of pyridine nitrogen in complex formation [29] is supported by the unaltered position of the pyridinic $\nu_{C=N}$ (1502 ± 2 cm^{-1}).

3.2. *^{1}H, ^{13}C, ^{119}Sn NMR spectra*

^{1}H NMR spectra of **1**–**6** exhibit no signal due to OH at 13.25–12.76 ppm, indicating metallation of OH [23]. Azomethine hydrogens at 9.93–8.32 ppm compared to parent Schiff bases (9.23–8.23 ppm) supports coordination of azomethine nitrogen to tin [30, 31].

^{13}C NMR spectra of **1**–**6** exhibit signals due to azomethine carbon at 160.5–158.9 ppm, shifted compared to that of parent Schiff bases (158.3–156.5 ppm), indicating coordination of azomethine nitrogen to tin [25, 32]. Signals at 163.8–161.1 ppm support formation of Sn–O–C bond. Complexes **4**–**6** show additional ^{13}C NMR signals at δ 67.06, 65.46, 64.74, and δ 26.77, 25.40, and 24.27 from THF.

The ^{119}Sn NMR chemical shifts for **1**–**6** are at −639.3 to −619.0 ppm, indicating six-coordinate tin [33–35].

3.3. *Mass spectra*

The mass spectra [4, 7, 36] exhibited molecular ion peaks (see experimental section) (*m/z*), characteristic of dimeric (**1**–**3**) and monomeric (**4**–**6**) complexes, respectively. Most of the fragments were observed as groups of peaks due to various isotopes of tin and chlorine. Mass spectra, their fragmentation pattern, and calculated isotopic distribution for the molecular ion peaks at *m/z* 873.3894, 847.5, 510.3, and 493.4, respectively, for **1**, **3**, **4,** and **6** are given (see Supplementary material.doc). These observations are in agreement with the molecular composition of the complexes. In mass spectra of **1** and **3** the molecular ion peak at *m/z* 873.38 [calculated mass for ($C_{28}Cl_6H_{24}N_2O_2Sn_2$); = 870.69], 847.5 [calculated mass for ($C_{24}Cl_6H_{18}N_4O_2Sn_2$); = 844.57] corresponds to the molecular mass supporting dimeric complexes. Important peaks were also observed at *m/z* 781.17, 731.49, 665.25, 569.17, 542.15, 493.31, 472.05, 438.08 (monomer), 436.08, 367.17, 322.20, 303.16, 263.16, 211.12, and 161.02 due to formation of various radicals $C_{14}H_{12}Cl_3NOSn^{\bullet}$, $C_7H_7^{\bullet}$, HCN, $CH_3^{\bullet}$, $Cl^{\bullet}$, $C_7H_6N^{\bullet}$, $C_6H_5O^{\bullet}$, $SnCl^{\bullet}$, and $SnCl_2^{\bullet}$ in **1**, whereas **3** showed prominent peaks at *m/z* 768.6, 745.5, 665.3, 660.3, 568.2, 543.2, 477.3, 425.2 (monomer), 380.1, 355.1, 321.2, 285.1, 248.2, 212.1, 186.1, and 138.0 due to formation of various radicals $C_{12}H_9Cl_3NOSn^{\bullet}$, $C_5H_4N^{\bullet}$, HCN, $Cl^{\bullet}$, $C_6H_5O^{\bullet}$, $SnCl^{\bullet}$, and $SnCl_2^{\bullet}$. Mass spectra of **4** and **6** showed molecular ion peak at *m/z* 510.3 [calculated mass for ($C_{18}Cl_3H_{20}NO_2Sn$); = 506.96] and *m/z* 493.4 [calculated mass for ($C_{16}Cl_3H_{17}N_2O_2Sn$); = 494.3996], which corresponds to molecular mass of the monomeric complexes. Important peaks were also observed at *m/z* 459.4, 431.1, 429.2, 391.3, 371.2, 355.1, 318.2, 297.2, 281.2, 246.2,

Table 1. Antibacterial activity[a] of Schiff bases and **1**–**3**.

	Zone of inhibition (in mm)			
Compounds	*E. coli*	*S. aureus*	*P. aeruginosa*	*S. epidermis*
o-smabH	6	6	7	12
p-smabH	8	7	9	13
sapH	14	17	13	9
[(μ-Cl)$_2$Sn$_2$(o-smab)$_2$Cl$_4$] (**1**)	19	11	16	12
[(μ-Cl)$_2$Sn$_2$(p-smab)$_2$Cl$_4$] (**2**)	12	11	12	14
[(μ-Cl)$_2$Sn$_2$(sap)$_2$Cl$_4$] (**3**)	17	19	18	12
Tetracyclin	22	20	22	22

[a]*In vitro*, agar well diffusion method, conc. 1 mg/mL in DMSO.

Table 2. Antifungal activity[a] of Schiff bases and **1**–**3**.

Compounds	Zone of inhibition (in mm)			
	A. niger	*C. albicans*	*T. rubrum*	*Microsporum*
o-smabH	12	9	12	11
p-smabH	13	6	8	14
sapH	11	13	7	9
$[(\mu\text{-Cl})_2Sn_2(\text{o-smab})_2Cl_4]$ (**1**)	19	16	14	13
$[(\mu\text{-Cl})_2Sn_2(\text{p-smab})_2Cl_4]$ (**2**)	19	14	16	16
$[(\mu\text{-Cl})_2Sn_2(\text{sap})_2Cl_4]$ (**3**)	13	11	12	14
Fluconazole	23	23	22	23

[a]*In vitro*, agar well diffusion method, conc. 100 μg/mL in DMSO.

214.1, 177.1, and 147.0 due to formation of various small molecules and radicals $C_6H_5^{\cdot}$, C_4H_8O, $CH_3^{\cdot}$, $Cl^{\cdot}$, HCN, and $Sn^{\cdot}$ in **4**, whereas **6** showed important peaks at *m/z* 462.3, 424.3, 380.0, 367.2, 355.2, 322.2, 289.1, 279.1, 263.1, 241.1, 211.1, 153.0, and 122 due to formation of various small molecules and radicals C_4H_8O, $Cl^{\cdot}$, $C_5H_4N^{\cdot}$ HCN, and $Sn^{\cdot}$.

3.4. *Biological activity*

The Schiff bases o-smab**H**, p-smab**H**, sap**H,** and their complexes (**1**–**3**) were tested for inhibitory effect on growth of different bacteria, *E. coli*, *S. aureus*, *P. aeruginosa*, *S. epidermidis,* and fungi, *A. niger*, *C. albicans*, *T. rubrum,* and *Microsporum* using the agar well diffusion method. The antibacterial and antifungal activities obtained for the Schiff bases and **1**–**3** are listed in tables 1 and 2, respectively. The complexes (**1**–**3**) displayed more activity against the same micro-organisms compared to the parent Schiff bases under identical experimental condition.

4. Conclusion

Six-coordinate chloride-bridged $Sn(\mu\text{-Cl})_2Sn$ dimeric and mononuclear complexes, $[(\mu\text{-Cl})_2Sn_2(\eta^2\text{-sb})_2Cl_4]$ and $[(sb)SnCl_3\cdot THF]$, have been synthesized and their structural features elucidated by IR, (^1H, ^{13}C, and ^{119} Sn) NMR, and mass spectral studies. The ligands and **1**–**3** were screened against bacteria and fungi as size of inhibition diameter. The Schiff bases show moderate activity and tin(IV) complexes (**1**–**3**) show appreciable activity.

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