

## Complexes of Sn(IV) with Schiff Bases Derived from Salicylaldehyde/Acetylacetone & *o*-Aminophenol, *o*-Aminobenzothiol & *o*-Aminobenzoic Acid\*

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A series of Sn(IV) complexes have been synthesized from stannic iodide and tridentate Schiff bases derived from salicylaldehyde (or acetylacetone) and *o*-aminophenol, *o*-aminobenzothiol and anthranilic acid. The ligands from *o*-aminobenzothiol contain benzothiazoline rings which are ruptured during formation of the metal chelate. Neutral hexa-coordinated octahedral structures have been proposed for the complexes, in which the di-anionic ligands act, probably, as planar tridentate ligands, forming bonds with Sn(IV) with ONO(or ONS) atoms in the vicinal planes.

**D**URING the course of our study on the acceptor property and complex-forming ability of stannic iodide, we have reported a series of diorganolead(IV)- and Sn(IV) complexes of bidentate and tetradentate Schiff bases<sup>1,2</sup>. The use of tridentate Schiff bases or similar ligands as the complexing agents for such compounds is practically unexplored; the only examples cited in literature describe the fully deprotonated penta-coordinated complexes,  $R_2ML$  [ $M = Sn(IV)$  or  $Pb(IV)$ ]<sup>3-5</sup>, octahedral complexes of the type  $M^{IV}(L)_3$  [ $M = Sn(IV)$ ,  $Si(IV)$  or  $Ti(IV)$ ]<sup>6,7</sup> and the partly deprotonated complex,  $[Et_3N][Cl_3Sn(SAPH)]$ <sup>6,8</sup>, where  $LH_2$  represents a binegative tridentate ligand and  $H_2SAP$  is the Schiff base derived from salicylaldehyde and *o*-aminophenol. In the present paper, we report a series of fully deprotonated Sn(IV) complexes with tridentate Schiff bases derived from salicylaldehyde and *o*-aminophenol ( $H_2SAP$ ); salicylaldehyde and *o*-aminobenzothiol ( $H_2SAB$ ); salicylaldehyde and *o*-aminobenzoic acid ( $H_2SAA$ ); acetylacetone and *o*-aminophenol ( $H_2AAP$ ); and acetylacetone and *o*-aminophenol ( $H_2AAB$ ).

As in the previous cases<sup>2</sup>, we first attempted to deprotonate the adduct of  $SnI_4$  and  $H_2SAP$  with tertiary bases (B) like triethylamine, pyridine, picolines, etc. In all the cases, partially deprotonated species<sup>6,8</sup> of the type  $[B][SnI_3(SAPH)]$  were obtained, even when the reactions were carried out with large excess of the tertiary bases (unpublished work). The preparation of the fully deprotonated species was, therefore, attempted by reacting the sodium salts of the Schiff bases and  $SnI_4$ , and this method gave satisfactory results.

### Materials and Methods

The ligands were prepared as usual by condensing the appropriate amines with salicylaldehyde or acetylacetone<sup>3,10,11</sup>. The Sn(IV) compounds were prepared by the following general procedure: A solution of the

ligand (5 mmoles in 10 ml of dry  $CH_3OH$ ) was mixed with 10 mmoles of  $NaOCH_3$  (prepared from 10 ml of dry methanol). To the resulting solution,  $SnI_4$  solution (2.5 mmoles in 15 ml of dry methanol) was added dropwise. The mixture was stirred vigorously during the addition in a dry  $N_2$  atmosphere. The complex began to precipitate when the addition was nearly complete. The precipitated product was filtered, washed with dry methanol and dried *in vacuo*. The complexes are all yellow in colour, stable at room temperature and fairly well soluble in DMF, DMSO and nitrobenzene.

Tin was estimated in the complexes gravimetrically as  $SnO_2$  and nitrogen by Duma's method. Conductance measurements were made on a Philips conductivity bridge (FR 9500 model). UV spectra were recorded in methanol ( $\sim 5 \times 10^{-5}M$ ) on a Hilger UVISPEK spectrophotometer and the IR spectra in the solid state (4000-600  $cm^{-1}$  region) were taken in an infrascan instrument (Hilger-Watt).

### Results and Discussion

Analytical data (Table 1) of the complexes correspond to the formula  $Sn(L)_2$  ( $H_2L$  being the general abbreviation for the ligands). The molar conduc-

TABLE 1 — ANALYTICAL AND CONDUCTANCE DATA OF THE COMPLEXES

Complex	m.p.	Found (Calc.), %		$\Delta M$ in DMF $ohm^{-1} cm^2$ mole <sup>-1</sup>
		Sn	N	
$Sn(SAP)_2$	> 350 (d)	21.9 (21.83)	5.25 (5.14)	30.6
$Sn(SAB)_2$	302 (d)	20.42 (20.64)	5.02 (4.85)	10.5
$Sn(SAA)_2$	> 350 (d)	20.04 (19.80)	4.92 (4.87)	41.5
$Sn(AAP)_2$	252	23.80 (23.75)	5.36 (5.59)	31.5
$Sn(AAB)_2$	317	21.84 (22.33)	5.54 (5.25)	15.5

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tance values of  $10^{-3}M$  solutions in nitrobenzene are insignificantly small. The conductance values in DMF solutions, however, indicated a slight dissociation of the complexes in this solvent, but the observed values were much less than those expected for 1:1 ionization<sup>12</sup>. The complexes are, therefore, regarded as neutral ones, viz.  $[Sn(L)_2]$ .

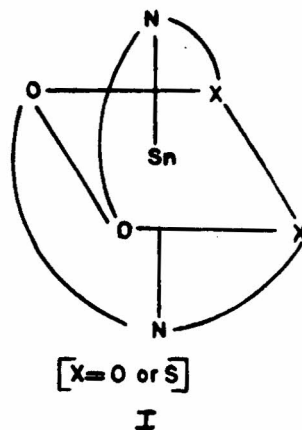
**Complexes with  $H_2SAP$ ,  $H_2SAA$  and  $H_2AAP$** —The Schiff bases  $H_2SAP$  and  $H_2SAA$  exist in the enolimine forms<sup>13</sup>, in which the phenolic hydroxyls are hydrogen-bonded to the lone-pair of the azomethine N-atom. A keto-enol tautomerism is most probable in the case of the ligand  $H_2AAP$ <sup>14,15</sup> which shows a medium broad band around  $3100\text{ cm}^{-1}$  assigned as the  $\nu O-H$  or ( $\nu N-H$ ), following the assignment made earlier<sup>16</sup>. The absence of any such band in the spectra of the complexes indicates the rupture of hydrogen-bonding and participation of both the O—H groups in complex formation. Shift of the phenolic  $\nu C-O$  (around  $1280\text{ cm}^{-1}$ )<sup>17</sup> towards higher frequency side by about  $15-20\text{ cm}^{-1}$  also suggests that the metal is covalently bonded in the complexes.

$\nu C=N$  of the ligands around  $1600\text{ cm}^{-1}$  shifts to lower frequency side showing the participation of the azomethine nitrogen in complex formation<sup>17</sup>. The large downward shift of about  $75\text{ cm}^{-1}$  in the case of  $Sn(AAP)_2$  may account for the increased single bond character of the double bonds on passing from the hydrogen-bonded structure to the covalently bonded metal chelates<sup>16,18,19</sup>.

In the UV region, while the  $\phi-\phi^*$  band of the phenyl group of the ligands around  $250\text{ nm}$  remains almost in the same position in their Na salts and the complexes, the longer wavelength band in the range  $250-270\text{ nm}$  representing the transition involving hydroxyl group and  $\pi$ -electrons of the  $C=N$  bond<sup>20</sup>, moves to higher wavelength side in the case of the Na salts and the complexes. The shift indicates an increase in conjugation between the azomethine group and the benzene ring which renders this part of the molecule more rigid and coplanar<sup>21</sup>. The K bands of the ligands<sup>20-22</sup> at  $300-350\text{ nm}$  are always less intense and move to longer wavelengths in the spectra of the Na salts and the complexes. The bathochromic shift of the enol bands in the present complexes suggests the participation of the anionic ligand molecules in complex formation and accounts for the partial S-character of the  $Sn-O$  bonds<sup>23,24</sup>. The quinonoid band (around  $440\text{ nm}$ ) of the ligands<sup>11,23</sup> is either absent or replaced by weak bands in the spectra of the complexes. The latter bands are probably due to an extra transition involving the metal-ligand bonds and suggest the planarity of the ligand molecules in the complexes<sup>20</sup>.

Thus, chelation results in the formation of a 6-membered and a 5-membered ring by deprotonation of two phenolic hydroxyls as well as by coordination through the azomethine nitrogen. The formation of 5-membered ring is stabilized by the 6-membered one and the planarity of the ligand as a whole is retained.

**Complexes with  $H_2SAB$  and  $H_2AAB$** —The ligands are only benzothiazoline derivatives with a hydrogen bond between thiazoline nitrogen and carbonyl



(or phenolic) oxygen (as indicated by the presence of  $\nu N-H$  bands near  $3300\text{ cm}^{-1}$  and by the absence of typical  $\nu S-H$  bands<sup>25,26</sup> near  $2550\text{ cm}^{-1}$ ). The weak band near  $3080\text{ cm}^{-1}$  is assigned to the stretching vibration of hydrogen-bonded O—H—N group in  $H_2SAB$ , while the strong band at  $1705\text{ cm}^{-1}$  in  $H_2AAB$  is assigned to  $\nu C=O$ , reduced in frequency due to hydrogen-bonding with thiazoline ring<sup>3</sup>. The spectra of the complexes neither show such bands nor any other band which can be assigned to  $\nu S-H$  or  $\nu N-H$ , indicating coordination of the (ONS) ligands in the deprotonated Schiff base form. Moreover, the weak bands around  $1620\text{ cm}^{-1}$  assigned to the thiazoline ring vibrations of the ligands are replaced by a very strong band at  $1615\text{ cm}^{-1}$  in  $Sn(SAB)_2$  and at  $1520\text{ cm}^{-1}$  in  $Sn(AAB)_2$  and these are attributed to  $\nu C=N$  of the Schiff base form in the chelates, since these are the highest absorption bands in the double bond region<sup>15,17,19</sup>. This is further corroborated by the appearance of a strong band at  $1300\text{ cm}^{-1}$ , assigned to the phenolic  $\nu C-O$  (bonded to metal via oxygen)<sup>15,17,19</sup>.

In general, the spectra of  $SnL_2$  and the Na salts of the ligands in the UV region, are markedly different from those of the free ligands. The remarkable similarity of the spectra of  $SnL_2$  and the Na salts of the present ligands with those of the complexes and the Na salts of the Schiff bases previously discussed, indicates the presence of similar anionic form in all the five complexes.

The above evidences strongly suggest that the condensed benzothiazoline form of the original ligands rearranges to the Schiff base enol-imine form in the presence of sodium methoxide and this then participates in the chelate formation with  $Sn(IV)$ . Such base-catalysed, metal-induced rearrangements for this type of ligands are not uncommon and the reaction probably proceeds via the attainment of an equilibrium between benzothiazoline form and anionic Schiff base form<sup>3,10,27</sup>.

The experimental data discussed above show that all the ligands are acting as potential tridentate ligands with  $Sn(IV)$  atom occupying 6-coordination positions in two different planes. PMR study by Biradar *et al.*<sup>7</sup> suggests that the azomethine N-atoms occupy *trans*-positions to each other in  $Ti(SAP)_2$ . In analogy, an octahedral configuration is suggested for  $SnL_2$  complexes, in which the two planar dianionic ligands are in two equatorial planes at right angles

to each other and the N-atoms of the azomethine groups occupy the axial positions as shown in structure (I).

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