

## Sn(IV) Compounds Interaction with Metal-Schiff Base Complexes

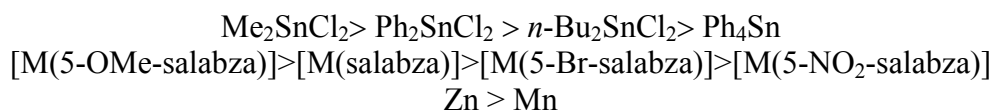
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### Abstract

The formation constants and Gibbs free energy for the interaction of  $R_nSnCl_m$  ( $n = m = 2$ ,  $R = Me, Ph, n-Bu$  or  $n = 4$ ,  $m = 0$ ,  $R = Ph$ ) compounds as acceptors, with ML complexes ( $H_2L = N,N'$ -bis(salicylidene)-2-aminobenzylamine (salabza- $H_2$ ) and its derivatives,  $M = Mn^{2+}$  or  $Zn^{2+}$ ), as donors in  $N,N'$ -dimethylformamide (DMF) as solvent were studied. These parameters were measured by using UV-vis spectrophotometry titration for 1:1 adduct formation of the selected complexes at  $25 (\pm 0.1) ^\circ C$  in the 200-500 nm regions. The trend of adduct formation constants between metal Schiff base complexes as donors and tin(IV) as acceptor decreases as follow:



**Keywords:** Formation constant; Manganese; Schiff base complex; Tin adduct; Zinc

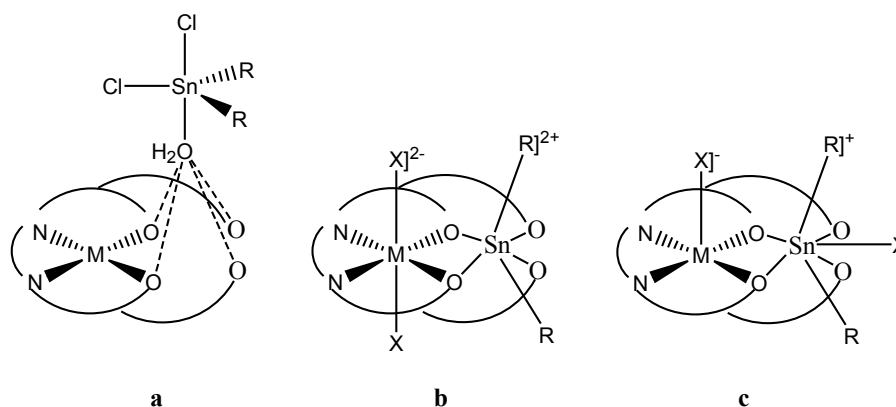
### Introduction

The observation that transition metal Schiff base complexes, [ML] ( $L =$  quadridentate Schiff base), can act as neutral donor ligands has been led to several investigations of their interactions with Lewis acids, specially tin compounds [1-11]. The results of X-ray diffraction analyses show that the square planar geometry of metal in their Schiff base complexes changed to octahedral geometry in the 1:1 adducts and the tin atom in these adducts have trigonal bipyramid, octahedral or pentagonal bipyramid geometries [4,5,7]. *Cunningham et al.* [5] have shown that the presence of methoxy substituents in the 3,3' positions of the metal salicylidimine ligands markedly alters the nature of the

addition complexes that they form with diorganotin(IV) Lewis acids and generally two types of complexes may be resulted. When the linking of the salicylidimine fragments is a two carbon atom chain such as ethylene group, aqua adducts of the diorganotin(IV) species are formed, with the donor water molecule held to the metal salicylidimine complex by hydrogen bonding interactions, as shown schematically in Fig. 1(a). When the chain contains three or four carbon atoms, diorganotin cations ( $SnR_2$ ) $^{2+}$  or ( $SnR_2X$ ) $^+$  ( $X =$  halogen or pseudohalogen) are generated, the tin atom of which in all cases lies in the plane of, and engages in donor bond formation with, the four Schiff- base oxygen atoms, as shown in Figures 1(b) and (c).

The adducts of vanadyl (IV) Schiff base complexes

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**Figure 1.** Schematic representation of the structures of the adducts from the reactions of  $\text{SnR}_2\text{X}_2$  ( $\text{R}$  = organo group;  $\text{X}$  = halide, thiocyanate, or nitrate) with divalent metal ( $\text{M}$ ) 3-methoxysalicylaldehyde complexes. Dotted lines signify hydrogen bonding interactions [5]. When the linking of the salicylaldehyde fragments is (a) two (b) and (c) three or four carbon atom chain.

with diorganotin(IV)dichloride and triorganotin(IV) dichloride have been investigated by *Ng et al.* [9,10] In these adducts, vanadyl oxygen acts as a donor atom and tin center as acceptor has trigonal bipyramidal geometry.

*Inada et al.* [11] have determined the stability constants of complex formation between  $\text{Cu}(\text{Salen})$  and metal(I, II) ion in acetonitrile. Also, the equilibrium data have been reported for interaction of  $\text{Ni}(\text{II})$  Schiff base complexes with alkaline earth metals in acetonitrile solution [12].

However, apart from the data of previous works by *Asadi et al.* [13-18], equilibrium data are lacking, and the range of stability constants for such adduct has not been established. This paper describes thermodynamic studies of novel 1:1 adduct formation of organotin compounds ( $\text{Me}_2\text{SnCl}_2$ ,  $\text{Bu}_2\text{SnCl}_2$ ,  $\text{Ph}_2\text{SnCl}_2$  and  $\text{Ph}_4\text{Sn}$ ) as acceptors with  $\text{M}(\text{II})$ -salabza Schiff base complexes (salabza- $\text{H}_2$  =  $\text{N,N}'$ -bis(salicylidene)-2-aminobenzylamine and its derivatives,  $\text{M} = \text{Mn}, \text{Zn}$ ) as donors in DMF solvent. By comparing the thermodynamic properties of  $\text{M}(\text{II})$  Schiff base complexes, we aimed to investigate the effects of different electronic and steric behaviors.

## Materials and Methods

Salicylaldehyde, 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 5-nitrosalicylaldehyde, 2-aminobenzylamine,  $\text{Mn}(\text{OAc})_2 \cdot 4\text{H}_2\text{O}$ ,  $\text{Zn}(\text{OAc})_2 \cdot 2\text{H}_2\text{O}$ ,  $\text{Ph}_2\text{SnCl}_2$ ,  $\text{Me}_2\text{SnCl}_2$ ,  $n\text{-Bu}_2\text{SnCl}_2$ ,  $\text{Ph}_4\text{Sn}$ , methanol, chloroform,  $\text{N,N}'$ -dimethylformamide were purchased from Fluka, Aldrich, Alfa Aesar or Acros and used without further purification. The electronic absorption spectra were recorded using a Rayleigh UV-1600 spectrophotometer.

## Synthesis of Schiff Base and Metal Complexes

The synthesis of the salabza- $\text{H}_2$  ligands was achieved by Schiff base condensation of a diamine with the appropriate aldehyde according to literature method [19].

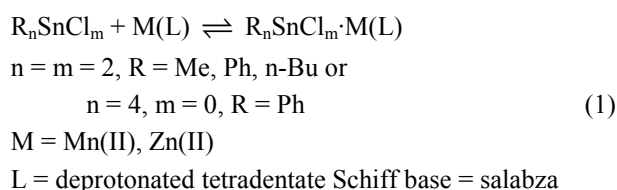
The metal complexes used in this study were readily prepared by reaction of salabza- $\text{H}_2$  with  $\text{M}(\text{OAc})_2 \cdot n\text{H}_2\text{O}$  in the molar ratio of 1:1 in reflux conditions according to previously published method [19].

## Molar Ratio Method

For the purpose of performing the molar ratio method [20], a series of solutions were prepared in which the complex concentration ( $1 \times 10^{-4} \text{M}$ ) has kept constant, while that of the organotin concentration ( $5 \times 10^{-6} - 2 \times 10^{-4} \text{M}$ ) has been varied for covering the molar ratios  $[\text{Sn}]/[\text{ML}] = 0.0-2.0$ . The spectra of all prepared solutions have been recorded within the wavelength range 200–500 nm. The relationship between the specific absorbance and molar ratio ( $[\text{Sn}]/[\text{ML}]$ ) for the different formed complexes in solution is plotted.

## Equilibrium Measurements

The adducts were obtained from the reaction of acceptors with donors, according to equation 1:



A solution of each M(II) Schiff base complex in DMF with concentration about  $10^{-4}$ M was prepared. In a typical measurement, 3 mL of this solution was transferred into the thermostated cell compartment of the UV-visible instrument, which was kept at constant temperature ( $25^{\circ}\text{C}$ ) by circulating water and was titrated by excess of the organotin compounds. The titration was performed with addition of aliquots of the titrant with a Hamilton  $\mu\text{L}$  syringe to the M(II) Schiff base complex.

The absorption measurements were carried out at various wavelengths where the difference in absorption was the maximum after the equilibrium was achieved. The formed adduct shows absorption different from the donor, while the acceptor shows no absorption at these wavelengths. As an example, the variation of the electronic spectra for  $[\text{Zn}(5\text{-Br-salabza})]\cdot 2\text{H}_2\text{O}$ , titrated with  $\text{Me}_2\text{SnCl}_2$  at  $25^{\circ}\text{C}$  in DMF was shown in Figure 2. The isosbestic points show that there is only one reaction in equilibrium. The same procedure was followed for other systems.

## Results and Discussion

### Electronic Spectra

The electronic spectra of the Schiff bases in solution show a relatively intense band in the 260–262 nm region assigned to  $\pi\text{-}\pi^*$  transitions that overlapped with  $n\text{-}\pi^*$  electronic transitions, and a low intensity absorption in the 316–355 nm which can be ascribed to the transition within the whole molecule essentially as intramolecular charge transfer (CT) interaction. Complexation with M(II) results in significant changes of the spectra between 300–450 nm which can be ascribed to MLCT bands [19].

Upon interaction of metal complexes with organotin, the original absorption of metal Schiff-base complexes changed and new peaks appeared (Fig. 2). Changes in electronic spectra show that formation of adducts causes a blue shift in the MLCT transition. The clear isosbestic points in Figure 2 represent adducts formation in solution.

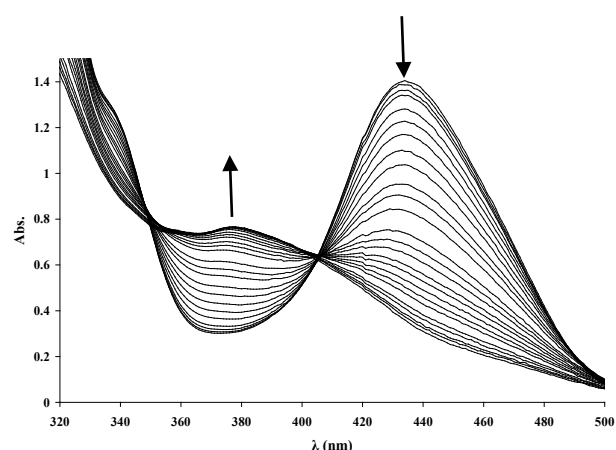
### Stoichiometry Evaluation, Formation Constants and Gibbs Free Energy Interpretations

Molar ratio (MR) [20] method to evaluate the stoichiometry of adducts in solution have been applied. It is evident that, the relationship obtained for the MR method are characterized by one breakdown located at the molar ratio  $[\text{Sn}]/[\text{ML}]$  equals to 1. This indicates that the stoichiometry ratio of the complexes in solution is 1:1 (Sn:ML).

The thermodynamic parameters are useful tools to study the interactions between donor and acceptor species and understand the relative stability of the formed adduct. The formation constant of the metal complexes with organotin compounds were calculated using the well-known SQUAD program [21,22], which was designed to calculate the best value for the formation constant of the proposed equation model (Eq. 1) by employing a non-linear, least-squares approach. Also the free energy change  $\Delta G^{\circ}$  of the complexes formed were calculated from  $\Delta G^{\circ} = -RT \ln K$  at  $25^{\circ}\text{C}$ .

In continuing of previous studies [13-18], we elucidated the steric and the electronic effects of a number of metal Schiff base complexes, and the organotin(IV) compounds, on the formation constant and the Gibbs free energy of the adduct formation. The results showed that the interaction between donors and acceptors depends on the type of the Schiff bases, metals and the organo groups on the tin(IV). It is useful to mention that, Sn(IV) compounds are Lewis acids with free coordination sites, and the reaction with Lewis bases leads to electronic and steric saturation of Sn center. According to the literature, all of these compounds are organotin aqua adducts with donor water molecule engaged in hydrogen bonding interactions with the phenolic oxygen atoms of the divalent metal Schiff base [4,5,8].

Previously, it has been shown that in nonpolar and weakly polar solvents such as chloroform and anisole, the water molecule stay coordinated in the adduct formed (Fig. 1a); but in polar solvents such as methanol and DMF, the tin atom can directly coordinate the phenolic oxygen of the donor (Fig. 1b) [15].



**Figure 2.** Spectrophotometric titration of  $[\text{Zn}(5\text{-Br-salabza})]\cdot 2\text{H}_2\text{O}$  ( $1 \times 10^{-4}$ M) with various amounts of  $\text{Me}_2\text{SnCl}_2$  ( $5 \times 10^{-6}$ – $2 \times 10^{-4}$ M) in DMF at  $25^{\circ}\text{C}$ .

**Table 1.** The formation constants,  $K_{av}$  ( $L \cdot mol^{-1}$ ), for metal Schiff base complexes with organotin compounds in DMF solvent at 25°C

	$Me_2SnCl_2$	$Ph_2SnCl_2$	$Bu_2SnCl_2$	$Ph_4Sn$
$[Zn(5-OMe-salabza)].CH_3OH$	5.06 ( $\pm 0.01$ )	4.66 ( $\pm 0.01$ )	4.27 ( $\pm 0.01$ )	2.81 ( $\pm 0.02$ )
$[Zn(salabza)].2H_2O$	4.53 ( $\pm 0.03$ )	4.45 ( $\pm 0.02$ )	4.22 ( $\pm 0.01$ )	2.78 ( $\pm 0.08$ )
$[Zn(5-Br-salabza)].2H_2O$	4.44 ( $\pm 0.11$ )	4.31 ( $\pm 0.01$ )	4.19 ( $\pm 0.07$ )	2.65 ( $\pm 0.08$ )
$[Zn(5-NO_2-salabza)].2CH_3OH$	3.99 ( $\pm 0.06$ )	3.45 ( $\pm 0.11$ )	3.32 ( $\pm 0.05$ )	2.45 ( $\pm 0.05$ )
$[Mn(5-OMe-salabza)].2CH_3OH$	4.98 ( $\pm 0.07$ )	4.60 ( $\pm 0.08$ )	4.10 ( $\pm 0.06$ )	2.80 ( $\pm 0.01$ )
$[Mn(salabza)].2H_2O$	4.49 ( $\pm 0.05$ )	4.14 ( $\pm 0.04$ )	4.00 ( $\pm 0.08$ )	2.74 ( $\pm 0.01$ )
$[Mn(5-Br-salabza)].2H_2O$	4.39 ( $\pm 0.08$ )	4.11 ( $\pm 0.08$ )	4.00 ( $\pm 0.07$ )	2.27 ( $\pm 0.02$ )
$[Mn(5-NO_2-salabza)].H_2O$	3.73 ( $\pm 0.02$ )	3.37 ( $\pm 0.05$ )	2.98 ( $\pm 0.02$ )	2.19 ( $\pm 0.08$ )

**Table 2.**  $\Delta G_{av}^\circ$  ( $kJ \cdot mol^{-1}$ ), values for metal Schiff base complexes with organotin compounds in DMF solvent at 25°C

	$Me_2SnCl_2$	$Ph_2SnCl_2$	$Bu_2SnCl_2$	$Ph_4Sn$
$[Zn(5-OMe-salabza)].CH_3OH$	-28.87 ( $\pm 0.03$ )	-26.59 ( $\pm 0.03$ )	-24.37 ( $\pm 0.03$ )	-16.03 ( $\pm 0.05$ )
$[Zn(salabza)].2H_2O$	-25.84 ( $\pm 0.07$ )	-25.38 ( $\pm 0.05$ )	-24.07 ( $\pm 0.03$ )	-15.86 ( $\pm 0.20$ )
$[Zn(5-Br-salabza)].2H_2O$	-25.32 ( $\pm 0.27$ )	-24.58 ( $\pm 0.03$ )	-23.90 ( $\pm 0.17$ )	-15.11 ( $\pm 0.20$ )
$[Zn(5-NO_2-salabza)].2CH_3OH$	-22.76 ( $\pm 0.15$ )	-19.68 ( $\pm 0.27$ )	-18.94 ( $\pm 0.12$ )	-13.97 ( $\pm 0.12$ )
$[Mn(5-OMe-salabza)].2CH_3OH$	-28.40 ( $\pm 0.17$ )	-26.23 ( $\pm 0.20$ )	-23.38 ( $\pm 0.15$ )	-15.97 ( $\pm 0.02$ )
$[Mn(salabza)].2H_2O$	-25.61 ( $\pm 0.12$ )	-23.61 ( $\pm 0.10$ )	-22.81 ( $\pm 0.20$ )	-15.62 ( $\pm 0.02$ )
$[Mn(5-Br-salabza)].2H_2O$	-25.04 ( $\pm 0.20$ )	-23.44 ( $\pm 0.20$ )	-22.81 ( $\pm 0.17$ )	-12.95 ( $\pm 0.05$ )
$[Mn(5-NO_2-salabza)].H_2O$	-21.27 ( $\pm 0.05$ )	-19.22 ( $\pm 0.12$ )	-17.00 ( $\pm 0.05$ )	-12.49 ( $\pm 0.20$ )

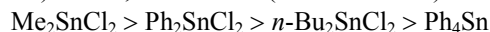
### The Acceptor Properties of Organotin Compounds

Four organotin compounds i.e. dimethyltin dichloride, dibutyltin dichloride, diphenyltin dichloride and tetraphenyltin have been examined in this work. The electronic and the steric factors can govern the formation process of adducts.

The following trend of acidic strength has been shown by Colton *et al.* [23]:  $SnCl_4 > RSnCl_3 > R_2SnCl_2 > R_3SnCl > R_4Sn$ . Replacing of an electron withdrawing chloride by electron donating methyl group compensates some of electron deficiency of the central tin(IV) atom and makes it a weaker Lewis acid. On the other hand, referring to the reported equilibrium constants for interaction of trialkyltin(IV) chlorides with pyrazine, we can see a good instance for influence of steric effect of alkyl groups on adduct stabilities [24]:  $Me_2SnCl_2 > Et_2SnCl_2 > n-Pr_2SnCl_2 > n-Bu_2SnCl_2$ . By increasing in steric effect of the organo group, the steric hindrance is increased. This parameter decreases the approaching of the acceptor and the donor and decreases the adduct formation. These two factors administrate the acceptor properties of the central tin atom.

On the basis of what has been described above, the trend of adducts formation of Sn(IV) compounds toward metal(salabza), as is confirmed by  $\Delta G^\circ$  (25°C) and  $K_{av}$

(25°C) values, is as follow (Tables 1 and 2):



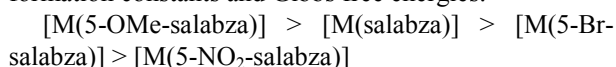
It is clear that the electron withdrawing groups (Ph) on the tin center makes  $Ph_2SnCl_2$  a stronger Lewis acid but steric hindrance of two bulky phenyls led to decrease of K values with respect to  $Me_2SnCl_2$ . This trend also indicates that replacing the methyl by a more bulky butyl group on the organotin(IV) compound causes the weakening of the interactions. The butyl group can affect the interaction in two ways; a more bulky butyl group makes adduct formation unfavorable because of its greater steric hindrance than the methyl group [24]. On the other hand, butyl groups have better electron releasing properties to reduce the acid strength of the organotin(IV) Lewis acid.  $Ph_4Sn$  has the lowest formation constants due to existence of four bulky phenyl groups.

### Donor Properties of the Metal(II) Schiff Base Complexes

For comprehensive study of organotin(IV) interaction with metal complexes, eight Mn(II) and Zn(II) Schiff base complexes were chosen. Two factors may affect on donor properties of the metal complexes:

### The Effect of the Substitution on Ligands

Tables 1 and 2 shows the following trend for the formation constants and Gibbs free energies:

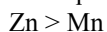


In the *para*-substituted Schiff-base ligands, the stability constants (K) varies with electronic effects of the substituents at positions 5,5'. Thus, the stability constants decrease according to the sequence OMe > H > Br > NO<sub>2</sub>. The more electron realising groups on the ligands makes it a strong Lewis base and therefore the increase in formation constant can be seen. Similar results have been reported previously for electrochemical properties of analogous Cu(II), Ni(II), V(IV), and Co(III) systems [25-27].

### Metal Effect

Zn(salabza) and Mn (salabza) complexes were selected to study the metal effect in the adduct formation between the divalent transition metal-salabza complexes and organotin(IV) compounds (Tables 1 and 2).

On the basis of the results, the formation constants for the adducts of M(salabza) complexes follow the below sequence:



In the studied systems, metal complexes act as donor species. By increasing the  $\pi$ -back bonding character of the metal atoms the donor ability of complexes were increased. Zn<sup>2+</sup> complex with fully occupied d orbitals (d<sup>10</sup> system), has low tendency to accept  $\pi$ -donation from ligands and has more ability to give  $\pi$ -back bond, therefore Zn complexes have higher formation constants than Mn complexes.

Although both of the Zn and Mn have low electron affinities, the value of electron affinity for Zn (-47 kJ/mol) is lower than Mn (0). The more electron affinity of central metal atom leads to decrease of donor properties of complexes and so decrease of adduct formation.

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