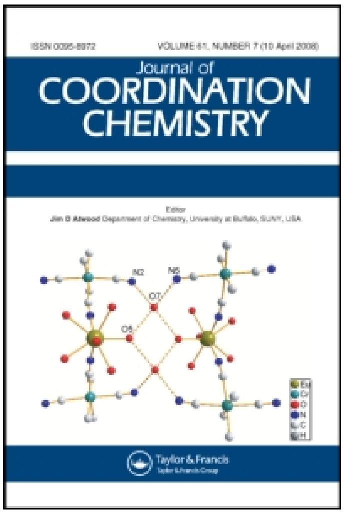

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Synthesis and thermodynamic studies of the dinuclear adducts between dimethyltin(IV) dichloride with SalenH$_2$ and M^{II}(Salen) complexes in chloroform

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A UV-Vis spectrophotometric study of adduct formation of SalenH$_2$ (**1**) and M^{II}(Salen), where M = Mn (**2**), Fe (**3**), Co (**4**), Ni (**5**) and Cu (**6**) as donors with Me$_2$SnCl$_2$ as acceptor have been investigated in chloroform. Adducts (**1a**–**6a**) have been characterized by ^{1}H, ^{13}C and ^{119}Sn NMR, IR and electronic spectroscopy and microanalysis. Formation constants and thermodynamic parameters were measured for 1 : 1 and 2 : 1 adducts at various temperatures (T = 278 to 308 K). The data refinement was carried out with the SQUAD 84 program. The trend of formation constants of M^{II}(Salen) complexes with Me$_2$SnCl$_2$ follows the order: Mn > Fe > Cu > Co > Ni. The formation constants for the free **1** and M^{II}(Salen) with Me$_2$SnCl$_2$ changes according to the following trend: M^{II}(Salen) > SalenH$_2$

Keywords: Divalent transition metal; Salen; Dimethyltin dichloride; Formation constants; Thermodynamic parameters

1. Introduction

Salen ligands, with four coordination sites and two axial sites open to ancillary ligands, are similar to porphyrins, but more easily prepared [1]. Schiff-base ligands are able to coordinate metals through imine nitrogen and another group, usually linked to the aldehyde, stabilizing many different metal ions in various oxidation states and controlling the performance of metals in a large variety of useful catalytic transformations. SalenH$_2$ is readily metalated by a variety of divalent metal cations. Salen derivatives of transition metals are used as biomimetic catalysts for oxygen atom transfers, as catalysts for enantioselective epoxidation reactions and for redox reactions [2–4].

In contrast to the extensive literature on the transition quadridentate Schiff-base metal complexes M(L) with a N$_2$O$_2$ donor atom set, rather little is known about the molecular interaction of these complexes with organic and inorganic acceptors. Few investigations on the molecular interaction between acceptor–donor systems have

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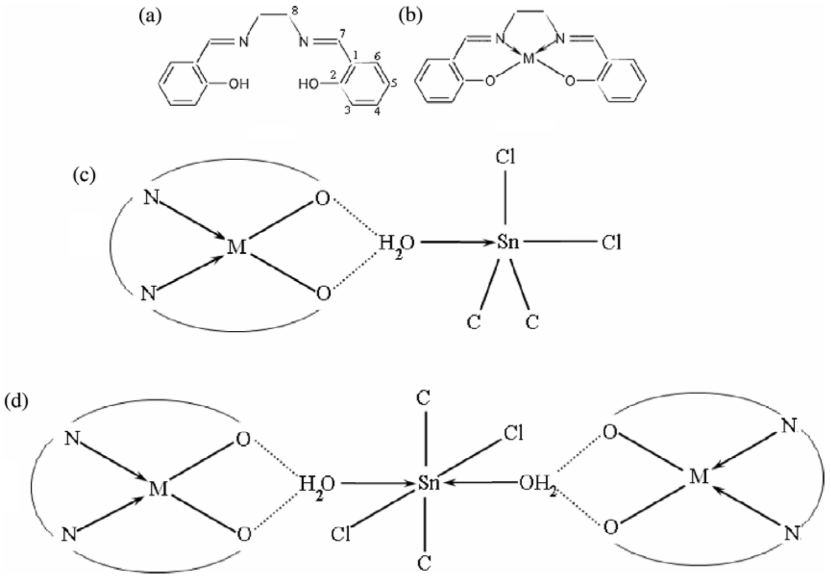

Figure 1. Structural representation of the (a) **1**, (b) **2**–**6** complexes, (c) **4a**–**6a** 1 : 1, and (d) **2** and **3** 1 : 2, M = Mn, Fe, Co, Ni and Cu. *C* = Me, *n*-Bu and Ph. In (c) M = Co, Ni and Cu, and in (d) M = Mn and Fe.

been done [5, 6]. X-ray diffraction analyses [7–11] show that square-planar or distorted tetrahedral geometry of transition metals in their Schiff-base complexes in polar solvent, such as DMF, changed to octahedral geometry by migration of halide ions from R_2SnCl_2 to the transition metal. In non polar or weakly polar solvents, such as chloroform, the geometry of the transition metal in the adduct is the same as the complexes. In chloroform, the geometry of the tin atom depends upon 1 : 1 or 2 : 1 (donor : acceptor) adducts, trigonal bipyramid and octahedral, respectively.

This article describes thermodynamic studies of 1 : 1 and 2 : 1 adducts of $SalenH_2$ and M^{II}(Salen) complexes with dimethyltin(IV) dichloride (see figure 1). Also, we investigate the effect of metals on the formation constant and the thermodynamic parameters of the adducts.

2. Experimental

2.1. *Apparatus and reagents*

UV-Vis measurements were carried out on a JASCO V-530 UV-Vis spectrophotometer equipped with a LAUDA Ecoline RE 104 thermostat. The ^{1}H and ^{13}C NMR spectra were recorded by a Bruker Avance DPX 250 and the ^{119}Sn NMR spectra were recorded on a Bruker Avance 400 MHz spectrometer. Microanalyses were carried out on a ThermoFinnigan Flash EA1112 instrument. IR spectra were recorded on a Shimadzu FTIR 8300 infrared spectrophotometer.

Salicylaldehyde, ethylenediamine, nickel acetate tetrahydrate, copper acetate monohydrate, cobalt acetate tetrahydrate, ferrous ammonium sulfate and manganese acetate

Table 1. Elemental analyses[a] of **1a**–**6a**.

Complex	C	H	N	Cl
$Me_2SnCl_2(Salen)\cdot H_2O$ (**1a**)	43.15 (42.90)	4.19 (4.40)	5.92 (5.56)	13.79 (14.07)
$2Mn(Salen)\cdot Me_2SnCl_2\cdot 2H_2O$ (**2a**)	45.73 (45.47)	4.53 (4.26)	6.59 (6.24)	7.54 (7.89)
$2Fe(Salen)\cdot Me_2SnCl_2\cdot 2H_2O$ (**3a**)	45.68 (45.37)	4.61 (4.26)	6.62 (6.23)	7.61 (7.88)
$Co(Salen)\cdot Me_2SnCl_2\cdot H_2O$ (**4a**)	38.23 (38.41)	4.07 (3.94)	5.12 (4.98)	12.87 (12.60)
$Ni(Salen)\cdot Me_2SnCl_2\cdot H_2O$ (**5a**)	38.12 (38.42)	4.29 (3.94)	5.23 (4.98)	12.93 (12.60)
$Cu(Salen)\cdot Me_2\ SnCl_2\cdot H_2O$ (**6a**)	37.79 (38.09)	3.62 (3.91)	5.31 (4.94)	12.13 (12.49)

[a] Calculated values in parentheses.

tetrahydrate were purchased from Merck, Fluka or Aldrich and used without further purification. Dimethyltin dichloride, methanol, ethanol, and chloroform were purchased from Merck and Fluka, distilled and purified before use.

2.2. *Synthesis of Schiff-base ligands and their divalent transition metal complexes*

Ligand **1** was prepared according to previously published methods [12]. Manganese, cobalt, nickel and copper Schiff bases were prepared using the corresponding metal(II) acetate $M(OAc)_2$ (M = Mn, Co, Ni, Cu) with **1**. Ni(Salen) (**5**) and Cu(Salen) (**6**) complexes were prepared from the corresponding metal acetate using a method described in the literature [13]. For Co(Salen) (**4**) and Mn(Salen) (**2**) the reaction was carried out refluxing in an inert Ar and N_2 atmosphere, respectively [14]. The Fe(Salen) (**3**) complex was synthesized through reaction between **1** and ferrous ammonium sulfate, $[(NH_4)_2Fe(SO_4)_2]$ under nitrogen [15]. The crystals were filtered, washed with cold ethanol and dried in a desiccator.

2.3. *Synthesis of the adducts of dimethyltin dichloride with metal Schiff-base complexes*

The adducts were prepared using the method described in the literature [6]. A solution of M^{II}(Salen) in chloroform was added to dimethyltin dichloride and the mixture was stirred for 4 h. Crystals of $Cl_2SnMe_2\cdot nM(Salen)\cdot nH_2O$ $\{n = 1$ for Cu, Ni and Co and 2 for Fe and Mn$\}$ (**2a**–**6a**) were filtered, recrystallized with chloroform and dried in a desiccator. The elemental analyses of **2a**–**6a** are collected in table 1.

2.4. *Synthesis of $Me_2SnCl_2(Salen)\cdot H_2O$ complex*

Dimethyltin dichloride (1 mmol) dissolved in boiling absolute ethanol (20 mL) was mixed with a hot solution of $SalenH_2$ (1 mmol) in the same solvent (30 mL) and the mixture was then refluxed for one hour [16]. Triethylamine (or KOH) in EtOH was added prior to the Sn(IV) treatment to facilitate the metalation process. On cooling to room temperature, yellow crystals of the $Me_2SnCl_2(Salen)\cdot H_2O$ (**1a**) were obtained, which were filtered off, washed with cold ethanol and dried in a desiccator over silica gel. The elemental analysis of **1a** is given in table 1.

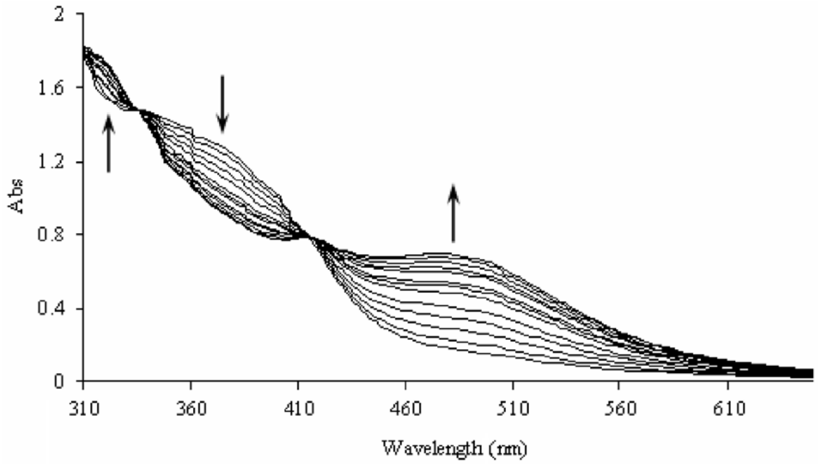

Figure 2. Spectrophotometeric titration of **3** [6.15×10^{-4} M] with Me_2SnCl_2 [$8.01 \times 10^{-8} - 8.01 \times 10^{-7}$ M] in chloroform ($T = 298.15$ K).

2.5. *Equilibrium measurements*

The adducts were obtained from the reaction of the acceptor with the donors according to equation (1):

$$Cl_2SnMe_2 + nM(Salen) \rightleftharpoons Cl_2SnMe_2 \cdot nM(Salen) \cdot H_2O \tag{1}$$

where $n = 1$ for Cu, Ni and Co and 2 for Fe and Mn.

The formation constant measurements were carried out by spectrophotometeric titration at $T = 278.15$, 288.15, 289.15, and 308.15 (± 0.1) K. In a typical measurement, 2.5 mL solution of M^{II}(Salen) (10^{-4} M) in chloroform was titrated with various excess concentrations of Me_2SnCl_2. The acceptor concentrations were varied one-to-ten fold of its initial concentration. In general the initial concentration depends upon the overall concentration that needs to complete the variation of the absorbance. UV-Vis spectra were recorded in the range 300–700 nm after 5 min (20 min for **6**) of each addition. The absorption measurements were monitored at various wavelengths in the 300 to 550 nm region where the difference in absorption between the M^{II} substrate and the product was the largest after the equilibrium was attained. As an example, the variation of the electronic spectra for **3** titrated with dimethyltin dichloride in chloroform at $T = 298.15$ K is shown in figure 2. The isosbestic points suggest that there are only two species in equilibrium. The same procedure was followed for other systems.

The average formation constants of the adducts were calculated in the selected range of spectra by using the well-known SQUAD 84 program [17] and the average thermodynamic parameters of the adducts were determined by the Van't Hoff equation (3),

$$\Delta G^{\circ}_{av} = \Delta H^{\circ}_{av} - T\Delta S^{\circ}_{av} \tag{2}$$

$$\ln K_{av} = \frac{-\Delta H^{\circ}_{av}}{RT} + \frac{\Delta S^{\circ}_{av}}{R} \tag{3}$$

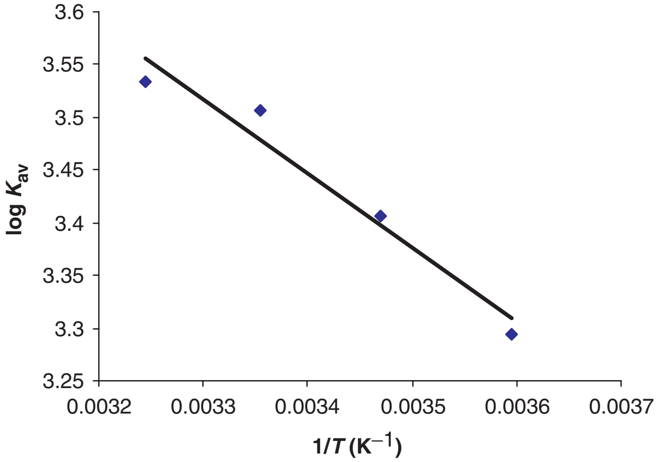

Figure 3. The linear plot for ln K_{av} of **4** titrated with Me_2SnCl_2 against $1/T$.

Table 2. UV-Vis bands λ_{max}($CHCl_3$/nm) of **1**–**6** and **1a**–**6a**.

Complex	$\lambda(\pi–\pi^*)$	$\lambda(n–\pi^*)$
1		318
1a		394
2	416	478
2a		486
3		362
3a		480
4		368
4a		446
5	344	412
5a	316	392
6		334
6a		368

where K_{av} is the average of the formation constant at various wavelengths, R is the gas constant and T is the temperature in Kelvin. Thermodynamic parameters of the studied complexes were obtained from the linear plots of ln K_{av} against $1/T$. Linear plots for ln K_{av} of **4** titrated with Me_2SnCl_2 against $1/T$ are shown in figure 3. The values of ΔH°_{av} and ΔS°_{av} were obtained from the slope and intercept, respectively. The Gibbs free energies, ΔG°, were calculated from equation (2).

3. Results and discussion

3.1. *Spectral characterization*

Electronic spectra. The spectra of the metal Schiff-base (table 2) complexes (figure 4) have an absorption between 300 and 490 nm assigned to MLCT band ($n–\pi^*$) [18].

The nickel Schiff-base complex has two peaks in this area. The first peak at ~330 nm, attributed to imino π–π* transition, is not significantly affected by adduct formation. The second band at 412 nm is assigned to n–π* transition (MLCT band) [19]. Upon the interaction of the Schiff-base complexes with dimethyltin dichloride, the original n–π* transition disappeared and new peaks appeared (see figure 2 and table 2).

NMR spectra. The ^{1}H, ^{13}C and ^{119}Sn NMR spectra of **1** and **5** and their adducts with dimethyltin dichloride are shown in tables 3 and 4. The paramagnetic manganese d^{5}, cobalt d^{7} and copper d^{9} complexes and the adducts (**2**, **2a**, **4**, **4a**, **6 and 6a**) have broadened NMR signals and are not reported [20–22].

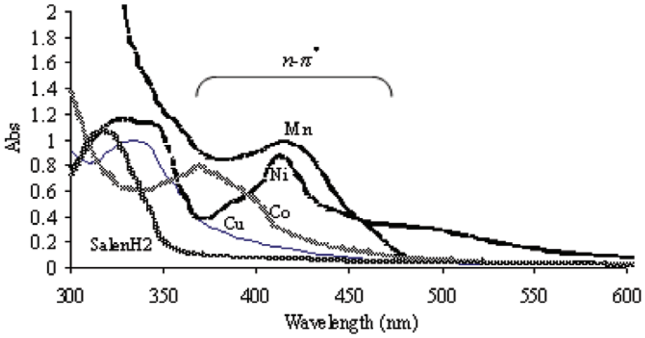

Figure 4. UV-Vis spectra of **2**–**6** and **1** [≈10^{-4} M] in chloroform ($T = 298.15$ K).

Table 3. ^{1}H NMR (250 MHz, CDCl$_3$, room temperature, TMS, ppm) bands of **1**, **1a**, **5** and **5a**.

Substrate	Me$_2$Sn (ppm)	^{2}J(^{1}H-^{119}Sn) (Hz)	Phenolic H	Aldimine H	Aromatic Hs
1	–	–	13.19	8.67	6.82–7.55
1a	1.23	84	–	8.49	6.80–7.34
5	–	–	–	7.39	6.47–7.19
5a	1.20	68	–	7.47	6.50–7.27

Table 4. ^{13}C NMR (62.90 MHz, CDCl$_3$, rt, TMS, ppm) and ^{119}Sn NMR (149.21 MHz, CDCl$_3$, rt, (CH$_3$)$_4$Sn, ppm) bands of **1**, **1a**, **5** and **5a**.

	1	**1a**	**5**	**5a**
Me$_2$Sn	–	13.10	–	13.21
^{a}C^{2} (2C, d)	166.78	160.81	166.49	162.09
^{a}C^{7} (2C, s)	166.78	135.75	132.37	137.03
^{a}C^{8} (2C, s)	58.79	57.17	59.75	58.45
Aromatic C	117.34, 118.54, 131.90, 133.18	113.86, 121.73, 132.19, 133.84	116.93, 118.66, 131.46	115.14, 121.20, 132.47, 133.83
^{119}Sn	–	90.13	–	7.09
J(^{1}3C-119Sn) Hz	–	1110.6	–	695.5
C-Sn-C(θ)	–	174.2°	–	137.8°

^{a}See figure 1.

The chemical shift observed for the OH protons in **1** (about 13.19 ppm) were not observed in metal complexes, confirming bonding of oxygen to the metal (C–O–M). The same result was confirmed by the IR spectra. The presence of a sharp singlet for the –C(H)=N proton in the Schiff bases (7.39–8.67 ppm) clearly indicates that the magnetic environment is equivalent for all such protons, suggesting the presence of a planar ligand in these complexes [23]. The aromatic protons appeared within the range of 6.47 to 7.55 ppm (table 3) and were weakly affected by adduct formation.

The formation of the adducts with dimethyltin dichloride was confirmed by the appearance of a sharp singlet for the Me_2Sn {(^{1}H 1.23 and 1.20 ppm), (^{13}C 13.36 and 13.21 ppm) and (^{119}Sn 90.13 and 7.09 ppm) for **1a** and **5a**, respectively}. Adduct formation causes a shift toward low field of the aldimine protons and phenolic protons (for ligand 1) (see table 3). Tin satellites were clearly observed in ^{13}C NMR spectra of the tin adducts. The ^{1}J coupling constants of the ^{13}C with ^{119}Sn nuclei were extracted from the the ^{13}C NMR spectra as 13 ppm. The Me–Sn–Me angle, θ, of the adducts, calculated (see table 4) from the ^{13}C NMR spectra using the Lockhart equation (4) [24], are in good agreement with the Cunningham *et al.* work [5–8].

$$|^1J| = 11.4(\theta^\circ) - 875 \tag{4}$$

IR spectra. The phenolic C–O stretching vibrations, at 1284 cm^{-1} in **1**, undergo a shift in the metal complexes (table 5) [25, 26], confirming the participation of oxygen in the C–O–M bond. A strong band at 1635 cm^{-1} in the free ligand is attributed to the C=N stretching vibration [27]. The ring skeletal vibrations (C=C) were consistent in all derivatives and weakly affected by complexation. The formation of the adducts shifts the C=N band and the phenolic C–O band toward higher frequencies (20–25 cm^{-1}) (table 5).

3.2. *The formation constants and the thermodynamic free energy calculations*

The formation constants of the various M^{II}(Salen) complexes with the dimethyltin(IV) dichloride were calculated using SQUAD 84 [16, 17].

Table 5. IR bands (cm^{-1}) of **1**–**6** and **1a**–**6a**.

Complex	(C=N) cm^{-1}	Ring skeletal (C=C) cm^{-1}	Phenolic (C–O) cm^{-1}
2	1634	1441–1595	1292
2a	1624	1443–1597	1292
3	1675	1445–1598	1309
3a	1630	1438–1612	1291
4	1651	1447–1603	1287
4a	1661	1450–1598	1312
5	1624	1450–1598	1250
5a	1649	1450–1600	1280
6	1632	1450–1595	1254
6a	1654	1448–1602	1284
1	1635	1458–1578	1284
1a	1643	1446–1607	1277

SQUAD is a program with the capability of refining formation constants of a general complex, $\mathrm{M}_m\mathrm{M}_l\mathrm{H}_k\mathrm{L}_n\mathrm{L}_q$, where m, l, n, $q > 0$ and k is positive for protons, negative for hydroxide ions or zero, employing a non-linear least squares approach. The data fed to SQUAD are absorption spectra, chemical composition (total concentrations of M, M′, L, L′, and pH) and a chemical model to describe the system. The residual sum (U) is calculated from equation (5):

$$\mathrm{U} = \sum\nolimits^{I}{}_{I}\sum\nolimits^{\mathrm{NW}}{}_{I}(\mathrm{A}_{i,k}^{\mathrm{Calcd}} - \mathrm{A}_{i,k}^{\mathrm{Obs}})^2 \tag{5}$$

where $\mathrm{A}_{i,k}$ is the absorbance value of the ith solution at the kth wavelength, given a total of I solutions and a grand total of NW wavelengths.

The formation constants and the free energy data are collected in tables 7 and 8. The average of the free energy values, $\Delta G^{\circ}_{\mathrm{av}}$, were calculated using equation (6). $\Delta G^{\circ}_{\mathrm{av}}$ values also were calculated using equation (2) and the results had less than one percent difference from that obtained using equation (6).

$$\Delta G^{\circ}_{\mathrm{av}} = -RT\ln K_{\mathrm{av}} \tag{6}$$

3.3. *Formation constants*

The synthesis and the structural characterization of metal Schiff-base complexes as a ligand with tin and organotin halides as acceptors were investigated [5–9], but there was no evidence for interaction of these compounds in solution. To study metal and metalation effects on acceptor–donor systems, the formation constants and thermodynamic parameters of the metal Schiff-base complexes and the free $\mathrm{SalenH_2}$ as donors with $\mathrm{Me_2SnCl_2}$ as acceptor were determined. The results show that the interaction between the donors and the acceptor are related to the type of metal.

3.3.1. Metal effect. The stability constant and the free energy parameter for the metal salen complexes and $\mathrm{SalenH_2}$ towards dimethyltin dichlorides were collected in tables 6 and 7. On the basis of the results, the formation of adducts for $\mathrm{M^{II}}$(Salen) complexes follow the sequence below:

$$\mathrm{Mn} > \mathrm{Fe} > \mathrm{Cu} > \mathrm{Co} > \mathrm{Ni}$$

Table 6. The formation constants, K_{av} ($\mathrm{L} \times \mathrm{mol}^{-1}$), for **1**–**6** with dimethyltin dichloride in chloroform at various temperatures.

Complex		$T = 278.15\,\mathrm{K}$	$T = 278.15\,\mathrm{K}$	$T = 298.15\,\mathrm{K}$	$T = 308.15\,\mathrm{K}$
2	K_1	$(2.63 \pm 0.01) \times 10^6$	$(1.00 \pm 0.21) \times 10^6$	$(8.13 \pm 0.09) \times 10^5$	$(2.96 \pm 0.06) \times 10^5$
	K_2	$(1.41 \pm 0.01) \times 10^6$	$(4.99 \pm 0.14) \times 10^6$	$(1.61 \pm 0.01) \times 10^7$	$(2.60 \pm 0.01) \times 10^7$
3	K_1	$(2.62 \pm 0.01) \times 10^5$	$(7.74 \pm 0.02) \times 10^5$	$(8.36 \pm 0.03) \times 10^5$	$(1.59 \pm 0.06) \times 10^6$
	K_2	$(6.92 \pm 0.03) \times 10^6$	$(6.30 \pm 0.01) \times 10^6$	$(6.03 \pm 0.01) \times 10^6$	$(5.75 \pm 0.01) \times 10^6$
6	K_1	$(5.53 \pm 0.71) \times 10^3$	$(7.68 \pm 0.15) \times 10^3$	$(9.66 \pm 0.22) \times 10^3$	$(1.03 \pm 0.16) \times 10^4$
4	K_1	$(1.97 \pm 0.08) \times 10^3$	$(2.55 \pm 0.17) \times 10^3$	$(3.21 \pm 0.24) \times 10^3$	$(3.41 \pm 0.17) \times 10^3$
5	K_1	$(4.18 \pm 0.10) \times 10^1$	$(5.26 \pm 0.13) \times 10^1$	$(5.37 \pm 0.16) \times 10^{:}$	$(6.04 \pm 0.13) \times 10^1$
1	K_1	$(2.52 \pm 0.09) \times 10^2$	$(1.96 \pm 0.09) \times 10^2$	$(1.52 \pm 0.09) \times 10^2$	$(1.38 \pm 0.08) \times 10^2$

$$\mathrm{M^{II}(Salen)} > \mathrm{SalenH_2}$$

The metal complexes are donors and increase in electron-withdrawing, and the π-acceptor qualities of the N_2O_2 donor atoms led to a decrease in donor ability of the metal salen complexes. The electronegativity (Pauling Scale) of the selected transition metals as 1.55, 1.83, 1.88, 1.91 and 1.90 for manganese, iron, cobalt, nickel and copper respectively, help us to interpret the above trend in the formation of adducts. The above trend also is confirmed by considering the $\mathrm{M^{II}}$–O and $\mathrm{M^{II}}$–N bond distances [28, 29]. Mean metal-ligand bond distances for isothiocyanate, pyridine, imidazole, water, and chloride, bound to Mn, Fe, Co, Ni and Cu in their 2+ oxidation states have been investigated by R. F. See *et al.* [28], as follows: $\mathrm{Mn} > \mathrm{Fe} > \mathrm{Co} \approx \mathrm{Cu} > \mathrm{Ni}$.

The bond distances order is in agreement with the electronegativity order. The more electronegative is the metal, the more it withdraws electrons and therefore less is the formation constant.

The coordination geometry of **6** is highly distorted square planar [30]. Distortion from square-planar to tetrahedral leads to decrease in the steric hindrance in approach of the tin acceptor and the donor. The formation constant for **6** is more than that for the less distorted **4** [31] and even more than that for the non-distorted **5**.

Comparing **1** with the metal salen complexes (see table 6), it is shown that the metals play an important role in the stability of the formed adducts. The contribution of the π-back donation from the metal toward the Salen empty π^* orbitals in the metal salen complex and the lack of the distortion by metalation render **1** to be a weaker donor than the metal Salen complexes.

3.3.2. The effect of temperature on the adduct formation.

In the case of **2** and **1** the formation constants decreased by increasing the temperature (see tables 6 and 8). For endothermic bond formation, in the case of **3**, **4**, **5** and **6**, the formation constants were increased by increasing the temperature (see tables 7 and 8). Thermal examination of **4** shows that the distorted square geometry around the cobalt probably changes to tetrahedral by increasing the temperature. The equilibrium of the planar via the tetrahedral is reversible, shifting toward the tetrahedral isomer with increasing temperature [32]. We recorded the spectra of **4** in chloroform in the temperature range $T = 278.15$–$328.15\,\mathrm{K}$. The typical 'planar' band of **4** at 368 nm was decreased

Table 7. $-\Delta G^\circ_{\mathrm{av}}$ ($\mathrm{kJ \times mol^{-1}}$), for **1**–**6** with dimethyltin dichloride in chloroform at various temperatures.

Complex		$T = 278.15\,\mathrm{K}$	$T = 278.15\,\mathrm{K}$	$T = 298.15\,\mathrm{K}$	$T = 308.15\,\mathrm{K}$
2	ΔG°_1	34.19 ± 0.04	31.96 ± 2.96	31.47 ± 0.15	29.14 ± 0.24
	ΔG°_2	32.74 ± 0.03	35.67 ± 0.04	38.38 ± 0.08	39.48 ± 0.05
3	ΔG°_1	28.85 ± 0.03	31.36 ± 0.04	31.54 ± 0.06	33.02 ± 0.50
	ΔG°_2	36.42 ± 0.08	36.21 ± 0.03	36.10 ± 0.02	35.99 ± 0.04
6	ΔG°_1	19.93 ± 1.11	20.69 ± 1.75	21.22 ± 2.11	21.36 ± 1.42
4	ΔG°_1	17.54 ± 0.30	18.14 ± 0.51	18.67 ± 0.62	18.81 ± 0.42
5	ΔG°_1	8.63 ± 0.09	9.16 ± 0.10	9.21 ± 0.12	9.48 ± 0.09
1	ΔG°_1	12.78 ± 0.20	12.20 ± 0.24	11.62 ± 0.30	11.39 ± 0.29

Table 8. ΔS°_{av} ($J \times K^{-1} \times mol^{-1}$) and ΔH°_{av} ($kJ \times mol^{-1}$), for **1**–**6** with dimethyltin dichloride in chloroform.

Complex		ΔS°_{av}	ΔH°_{av}
2	1 : 1	-50.57 ± 2.66	-48.15 ± 7.77
	2 : 1	115.39 ± 1.68	4.30 ± 0.49
3	1 : 1	246.36 ± 29.86	39.29 ± 8.73
	2 : 1	373.93 ± 26.70	70.98 ± 7.81
6	1 : 1	125.96 ± 9.05	14.98 ± 2.65
4	1 : 1	111.89 ± 6.93	13.50 ± 2.03
5	1 : 1	60.41 ± 6.30	8.08 ± 1.84
1	1 : 1	-7.22 ± 5.40	-14.74 ± 1.58

with increasing temperature. The distortion of planar to tetrahedral geometry favored the formation of adducts [33]; this form is a better ligand for coordination to tin compounds. Therefore the formation constants were increased by increasing the temperature for **4** as a ligand toward Me_2SnCl_2 as acceptor.

3.3.3. Thermodynamic parameters. The thermodynamic parameters ΔS° and ΔH° for the adducts of selected divalent transition metal salen complexes and $SalenH_2$ towards dimethyltin dichlorides are collected in table 8.

3.3.3.1. The heat of formation. ΔH° value and its sign are dependent on two factors: one is the heat of solvation, the other one is the heat of formation of the adduct [34]. In the metal salen series (except for manganese), the heat of formation decreased on decreasing the size of the central metal and is exothermic while liberation of the solvent molecules during adduct formation is endothermic. The solvation effect predominates (except for **2**). Changing the geometry from square planar or tetrahedral to octahedral for the donor and the acceptor, respectively [7, 8], play an important role in decreasing ΔH° values and its sign. In Mn and Fe systems the second step is more difficult and more endothermic than the first step. In the case of **1**, the formation of more crowded adduct with respect to the free ligand caused decrease in the solvation of the substrates. Therefore the sign of the enthalpy change in the **1** system is negative.

3.3.3.2. The entropy values. The ΔS° value and its sign also depend upon two factors: one is the difference in the number of particles of the initial and product complexes. The n for 1 : 1 systems studied is -1 and for 2 : 1 systems is -2 (ΔS° is negative). The second factor is the liberation of the solvent molecules from the solvation shells. This factor has positive contribution to ΔS° [34]. In the metal salen series (except for manganese), the first factor is the same but the second factor decreases with decreasing size of the central metal ion. Therefore the ΔS°_{av} values decreased through the series (see table 8). In the case of manganese ion because of its exothermic bond formation and its spherically symmetric configuration d^5, the first factor dominates the ΔS°_{av} value. Concerning the second step in the adduct formation for Mn^{II} and Fe^{II} systems, the liberation of more solvent molecules contributes more to the ΔS°_{av}.

In the case of $SalenH_2$, because of lack of the central metal ion, the liberation of solvent molecules during the adduct formation is less with respect to the M^{II}(Salen), therefore the sign of ΔS°_{av} is negative and its value is less.

4. Conclusions

By considering the formation constants and the $\Delta G^{\circ}_{\mathrm{av}}$ of the adduct formation for $\mathrm{M^{II}}$(Salen) complexes and the free $\mathrm{SalenH_2}$ as donors and dimethyltin(IV) dichloride as acceptor, the following conclusions have been drawn:

1. The trend of formation constants of the $\mathrm{M^{II}}$(Salen) complexes with $\mathrm{Me_2SnCl_2}$ decreases as follows:

$$\mathrm{Mn > Fe > Cu > Co > Ni}$$

2. The formation constants for a free $\mathrm{SalenH_2}$ and $\mathrm{M^{II}}$(Salen) with $\mathrm{Me_2SnCl_2}$ changes according to the following trend:

$$\mathrm{M^{II}(Salen) > SalenH_2}$$

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