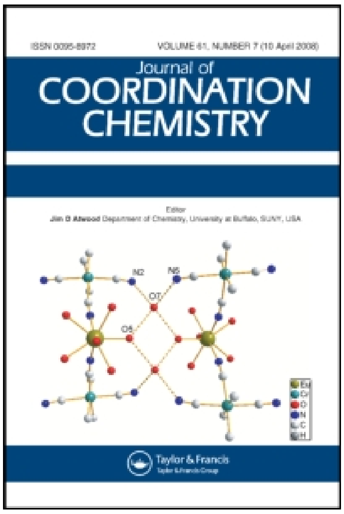

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Thermodynamic study of dinuclear adducts between copper(II) Salen-type complexes and organotin(IV) chlorides in acetonitrile

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Adduct formation between R_2SnCl_2 (R = methyl and phenyl) and $PhSnCl_3$ as acceptors and Cu(II) complexes of tetradentate Schiff-base ligands [CuL], where L = [Salen, bis(salicylaldehyde)ethylenediimine], [3-MeOSalen, *N*,*N′*-bis(3-methoxysalicylaldehyde)ethylenediimine], [5-MeOSalen, *N*,*N′*-bis(5-methoxysalicylaldehyde)ethylenediimine], [5-BrSalen, *N*,*N′*-bis(5-bromosalicylaldehyde)ethylenediimine], [salpn, *N*,*N′*-bis(salicylaldehyde)1,3-propanediimine], [Salophen, bis(salicylaldehyde)phenylenediimine], [3-MeOSalophen, *N*,*N′*-bis(3-methoxysalicylaldehyde)phenylenediimine], and [5-MeOSalophen, *N*,*N′*-bis(5-methoxysalicylaldehyde)phenylenediimine], as donors have been investigated in acetonitrile by UV-Vis spectrophotometric analysis. The formation constants and thermodynamic free energies were measured using UV-Vis titration for 1 : 1 adduct formation at various temperatures ($T = 293$–313 K). The trend of adduct formation for copper Schiff-base complexes with a given tin acceptor decreases as follows: Cu(5-MeOSalen) > Cu(Salen) > Cu(5-BrSalen); Cu(3-MeOSalen) > Cu(5-MeOSalen) > Cu(Salen); Cu(3-MeOSalophen) > Cu(5-MeOSalophen) > Cu(Salophen). The trend of the reaction of R_nSnCl_{4-n} acceptors toward a given copper Schiff-base complex is $PhSnCl_3 > Ph_2SnCl_2 > Me_2SnCl_2$. The reactivity of $PhSnCl_3$ toward Cu(Salen), Cu(Salpn), and Cu(Salophen) increases with increasing temperature.

Keywords: Copper; Schiff base; Organotin chloride; Formation constants; Adduct formation

1. Introduction

Metal complexes of Schiff bases derived from aromatic carbonyl compounds have been widely studied as metalloprotein models and asymmetric catalysts due to the versatility of their steric and electronic properties, which can be tuned by choosing appropriate amine precursors and ring substituents [1]. Schiff bases derived from salicylaldehyde and diamines, as *N*,*N′*-bis(salicylaldehyde)ethylenediamine (H_2Salen), constitute one of the most relevant synthetic ligand systems with importance in asymmetric catalysis. While providing easy access, they are of importance as catalysts for a broad range of reactions [2].

Several investigations have been done on the molecular structure of transition metal Schiff-base complexes as ligands in tin chemistry [3, 4]. X-ray diffraction analysis shows

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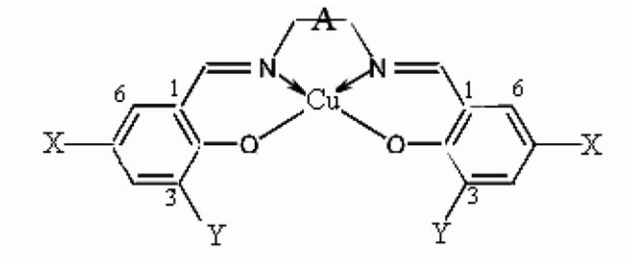

	A	X	Y
Salen	Et	H	H
Salpn	Pr	H	H
Salophen	Ph	H	H
3-MeOSalen	Et	H	MeO
5-MeOSalen	Et	MeO	H
5-BrSalen	Et	Br	H
3-MeOSalophen	Ph	H	MeO
5-MeOSalophen	ph	MeO	H

Figure 1. Structural representation of copper Schiff-base complexes.

that the square-planar geometry of nickel in its Schiff-base complexes changes to octahedral geometry in the 1 : 1 adducts, and the tin in those adducts has a tetrahedral and octahedral geometry [5].

Equilibrium data have been reported for Ni(II) Schiff-base complexes and for alkaline earth metals in acetonitrile [6]. Inada *et al.* [7] have determined stability constants of M(Salen) with metal(II, I) ions in acetonitrile. Ni(II) Schiff-base complexes with organotin(IV) chlorides were investigated previously [8–12].

The present article describes adduct formation of organotin(IV) chlorides with Cu(II) Salen-type N_2O_2 complexes, in which the copper complex is a neutral bi- and tetradentate ligand through its phenolic and methoxy oxygens in accord with previous findings [3–5]. This article describes spectral and thermodynamic studies of 1 : 1 adducts of organotin chlorides Me_2SnCl_2, Ph_2SnCl_2, and $PhSnCl_3$ as acceptors with Cu(II) Salen-type Schiff-base complexes, Cu(Salen), Cu(3-MeOSalen), Cu(5-MeOSalen), Cu(5-BrSalen), Cu(Salpn), Cu(Salophen), Cu(3-MeOSalophen), and Cu(5-MeOSalophen), as donor ligands in acetonitrile (figure 1). By comparing the spectral and thermodynamic properties of Cu(II) Schiff-base complexes, we investigate the effects of different electronic and steric factors.

2. Experimental

2.1. *Reagents*

Salicylaldehyde, 3-methoxysalicylaldehyde, 5-methoxysalicylaldehyde, 5-bromosalicylaldehyde, 1,2-ethylenediamine, 1,3-propanediamine, 1,2-phenylenediamine methanol,

ethanol, chloroform, acetonitrile, diphenyltin dichloride, phenyltin trichloride, and copper acetate tetrahydrate were purchased from Merck, Fluka, or Aldrich and used without purification. Dimethyltin dichloride was purchased from Merck and purified before use.

2.2. *Physical measurements*

UV-Vis measurements were carried out in a JASCO V-570 UV-Vis spectrophotometer equipped with a LAUDA ecoline RE 104 thermostat. The NMR spectra were recorded by a Bruker Avance DPX 250 MHz spectrometer. The IR spectra were recorded by a Shimadzu FTIR 8300 infrared spectrophotometer.

2.3. *Synthesis of Schiff bases and their copper complexes*

The Schiff bases used in this study were prepared according to previously published methods [13]. Copper Schiff-base complexes were prepared using a method described [14]. The crystals were filtered, washed with cold ethanol, and dried in a desiccator over phosphorus(V) oxide.

2.4. *Equilibrium measurements*

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

$$\mathrm{Cu(SB)} + \mathrm{R}_n\mathrm{SnCl}_{4-n} \rightleftarrows \mathrm{R}_n\mathrm{SnCl}_{4-n}\mathrm{Cu(SB)} \qquad (1)$$

where SB = [Salen], [3-MeOSalen], [5-MeOSalen], [5-BrSalen], [Salophen], [3-MeOSalophen] and [5-MeOSalophen] and $\mathrm{R}_n\mathrm{SnCl}_{4-n} = \mathrm{Me}_2\mathrm{SnCl}_2$, $\mathrm{Ph}_2\mathrm{SnCl}_2$, and PhSnCl_3. The proposed structures [(a) and (b)] for adducts are shown in figure 2; solid-state structures of the adducts were determined by X-ray reported previously [5, 15]. Equilibrium constant measurements were carried out by spectrophotometric titration at 25(±0.1)°C. In a typical measurement, 2.5 mL solution of Cu(SB) (10^{-5} M) in chloroform was titrated with $\mathrm{R}_n\mathrm{SnCl}_{4-n}$($10^{-5}$–$10^{-3}$ M). The acceptor concentrations were varied 1–20 fold in excess. UV-Vis spectra were recorded in the range 300–700 nm about 7 min after each addition. Absorption measurements were monitored at various wavelengths from 300 to 450 nm where the difference in absorption between the Cu(II) substrate and the product was the largest after equilibrium was attained. As an example, variation of the electronic spectra for Cu(Salen), titrated with PhSnCl_3 in acetonitrile is shown in figure 3. The isosbestic points suggest only two species in equilibrium. The same is valid for other systems. The formation constants of the adducts were calculated by using the well-known Ketelaar equation [16] using the SQUAD 84 program [17, 18]. Thermodynamic free energies (ΔG°) of the adducts were obtained according to the literature [11]. Thermodynamic parameters, ΔS° and ΔH°, of the adducts were determined by the Van't Hoff equation [11].

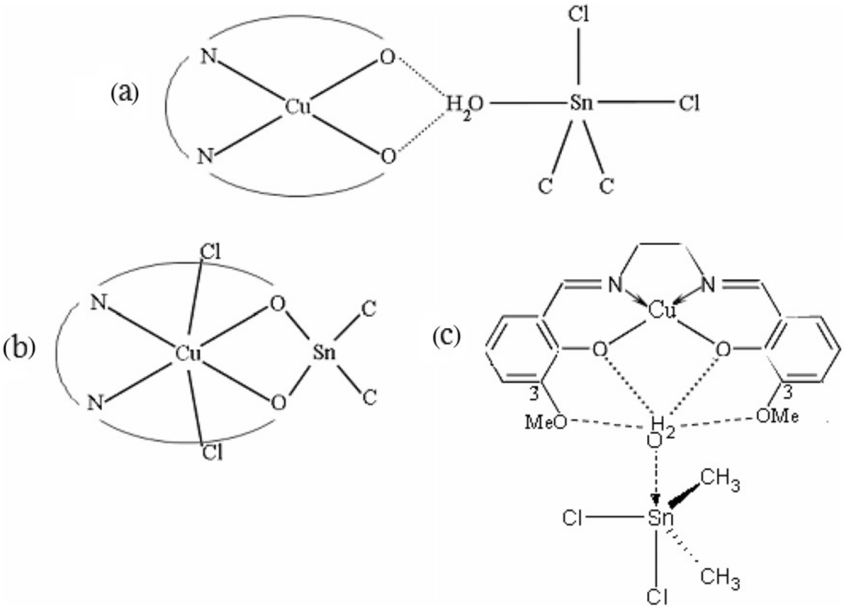

Figure 2. Schematic representation of the structure of adducts Me_2SnCl_2 with copper Schiff-base complexes.

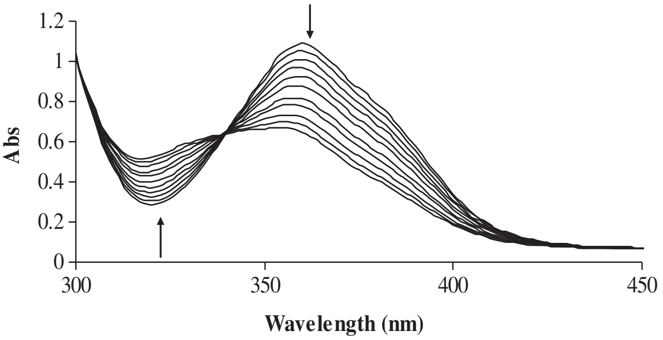

Figure 3. Spectrophotometric titration of Cu(Salen) (8.5×10^{-5} M) with $PhSnCl_3$ (9.84×10^{-6} to 1.97×10^{-4} M) in acetonitrile ($t = 25°C$).

3. Results and discussion

3.1. *Spectral characterization*

3.1.1. Electronic spectra. The electronic spectra of the Schiff bases in solution show a relatively intense band in the 300–380 nm region, π–π^* transition, and a low intensity absorption in the 360–500 nm region, involving n–π^* excitation [19]. Complexation with Cu(II) results in two significant changes of the spectra between 300–500 nm of MLCT and π–π^* absorption bands [20]. Upon interaction of copper Schiff-base complexes with organotin chlorides, the original absorption of copper Schiff-base complexes changed and new peaks appeared (figure 3). Changes in electronic spectra show that formation of adducts causes a blue shift in the MLCT transition. The clear isosbestic points in figure 3 represent the adduct formation in solution.

3.1.2. IR spectra. The strong IR band between 1640 and 1600 $\mathrm{cm^{-1}}$ is assigned to the C=N band characteristic for Schiff bases. The ring skeletal vibrations (C=C) of Schiff bases were in the region of 1440–1600 $\mathrm{cm^{-1}}$. The phenolic C–O stretching vibrations appeared at 1250–1300 $\mathrm{cm^{-1}}$ in the Schiff bases. All the vibrations undergo a shift toward lower frequencies (10–15 $\mathrm{cm^{-1}}$) in the copper complexes, in agreement with previous investigations [21, 22].

3.2. *Formation constants and free energy calculations*

The formation constants of the various Cu(II) Schiff-base complexes with the organotin(IV) chlorides were calculated using the Ketelaar equation [16]

$$\left(C_\mathrm{A}^\circ C_\mathrm{D}^\circ\right)/\left(A - A_\mathrm{A}^\circ - A_\mathrm{D}^\circ\right) = (1/(\varepsilon_\mathrm{C} - \varepsilon_\mathrm{A} - \varepsilon_\mathrm{D}))\left[(1/K) + \left(C_\mathrm{A}^\circ C_\mathrm{D}^\circ\right)\right] \tag{2}$$

where C_A° and C_D° are the initial concentrations ($\mathrm{mol\,L^{-1}}$) of the acceptor and donor, respectively; A is the optical density of the solution including the acceptor and the donor; A_A° and A_D° are the optical densities of the pure acceptor and pure donor in the solution of concentrations C_A° and C_D°; ε_C, ε_A, and ε_D are the molar absorption coefficients ($\mathrm{L\,mol^{-1}\,cm^{-1}}$) of the complex, the acceptor, and the donor, respectively; K is the formation constant of the formed complex and the cell optical path length is 1 cm.

A plot of $C_\mathrm{A}^\circ \times C_\mathrm{D}^\circ/(\mathrm{A} - A_\mathrm{A}^\circ - A_\mathrm{D}^\circ)$ *versus* $(C_\mathrm{A}^\circ + C_\mathrm{D}^\circ)$ should produce a straight line if only a 1 : 1 complex is formed, while a mixture of 1 : 1 and 1 : 2 or only 1 : 2 complex in a system would lead to a curve. The formation constants of the studied Cu(II) Schiff-base adducts were calculated from the ratio of the slope to the intercept by the least-square method using Microsoft Excel 2003. The K measurements were repeated at least twice and were reproducible. Linear plots for Cu(Salpn) titrated with $\mathrm{Ph_2SnCl_2}$ at 25°C in acetonitrile are shown in figure 4, which signify that only a 1 : 1 adduct is formed. Similar plots are obtained for other systems. The formation constants and the thermodynamic free energies are collected in tables 1–3.

3.3. *Formation constants*

Synthesis and structural characterization of copper Schiff-base complexes as a ligand with tin and organotin halides were widely investigated [3, 4], but there is no evidence for interaction of these compounds in solution or their tendency to adduct formation. With the goal to study electronic and steric parameters of the donors and acceptors on formation constants and the thermodynamic free energy, the interaction of the copper Schiff-base complexes as donors with organotin halides as acceptors were examined. Formation constants and the interaction between donors and acceptors are related to the type of Schiff base, organotin halides, and temperature.

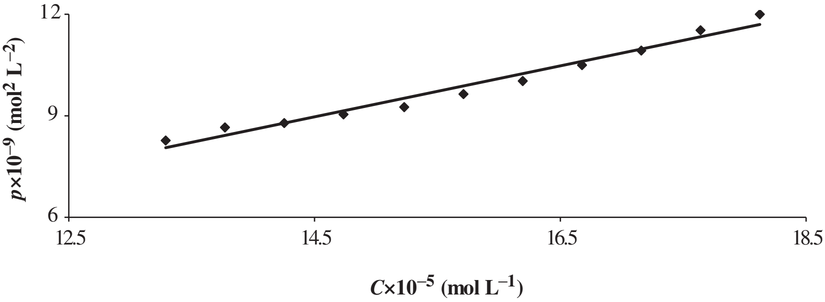

Figure 4. Ketelaar plots for Cu(Salpn) (9.90×10^{-5} M) with Ph_2SnCl_2 (4.84×10^{-5} to 9.68×10^{-3} M) at 25°C in acetonitrile, where $P = C^\circ_A \times C^\circ_D/(A - A^\circ_A - A^\circ_D)$ and $C = (C^\circ_A + C^\circ_D)$.

Table 1. Formation constants, K (L mol^{-1}), for copper Schiff-base (CuSB) complexes with organotin chlorides in acetonitrile at 25°C.

SB	$PhSnCl_3$	Ph_2SnCl_2	Me_2SnCl_2
Salen	$(16\pm0.5)\times10^3$	$(2.0\pm0.2)\times10^2$	$(2.5\pm0.1)\times10^1$
3-MeOSalen	$(42\pm2)\times10^3$	$(3.0\pm0.3)\times10^2$	$(110\pm1)\times10^1$
5-MeOSalen	$(30\pm2)\times10^3$	$(5.0\pm0.5)\times10^2$	$(4.0\pm0.1)\times10^1$
5-BrSalen	$(3.0\pm0.4)\times10^3$	$(0.6\pm0.1)\times10^2$	$(1.0\pm0.1)\times10^1$
Salpn	$(60\pm2)\times10^3$	$(5.0\pm0.5)\times10^2$	$(8.0\pm0.2)\times10^1$
Salophen	$(2.5\pm0.3)\times10^3$	$(3.0\pm0.5)\times10^2$	$(4.0\pm0.1)\times10^1$
3-MeOSalophen	$(10.0\pm0.5)\times10^3$	$(2.2\pm0.5)\times10^2$	$(25\pm3)\times10^1$
5-MeOSalophen	$(3.3\pm0.4)\times10^3$	$(7.5\pm0.7)\times10^2$	$(5.0\pm0.1)\times10^1$

Table 2. Formation constants, K (L mol^{-1}), for copper Schiff-base with $PhSnCl_3$ at different temperatures in acetonitrile.

	20	25	30	35	40
Salpn	$(26\pm2)\times10^3$	$(40\pm2)\times10^3$	$(60\pm2)\times10^3$	$(70\pm3)\times10^3$	$(75\pm3)\times10^3$
Salen	$(7.7\pm0.5)\times10^3$	$(8.7\pm0.7)\times10^3$	$(16.0\pm0.5)\times10^3$	$(22\pm1)\times10^3$	$(30\pm2)\times10^3$
Salophen	$(2.0\pm0.2)\times10^3$	$(2.2\pm0.2)\times10^3$	$(2.5\pm0.3)\times10^3$	$(4.3\pm0.4)\times10^3$	$(7.5\pm0.8)\times10^3$

Table 3. Thermodynamic parameter ΔH (KJ mol^{-1}), ΔS (J mol^{-1} K^{-1}), and ΔG (KJ mol^{-1}) for copper Schiff-base with $PhSnCl_3$ in acetonitrile.

	ΔH	ΔS	ΔG^a
Salen	56 ± 6	260 ± 20	$-(22.5\pm0.8)$
Salpn	41 ± 8	230 ± 30	$-(26.3\pm0.6)$
Salophen	50 ± 12	230 ± 40	$-(19.1\pm0.8)$

[a] At 25°C.

3.3.1. The acceptor properties of organotin chlorides. Dimethyltin dichloride, diphenyltin dichloride, and phenyltin trichloride show that formation constants toward the copper Schiff-base complexes change according to the trend:

$$PhSnCl_3 > Ph_2SnCl_2 > Me_2SnCl_2$$

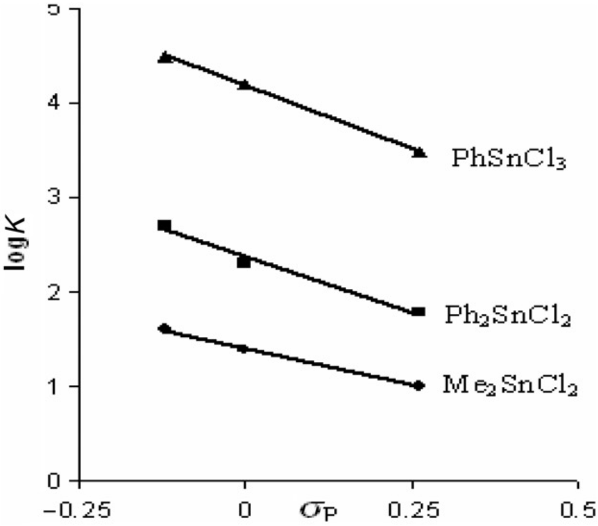

Figure 5. Linear correlation between para-substituent constants and adduct formation, log K *versus* σ_P, $PhSnCl_3$ ($r = 0.999$), Ph_2SnCl_2 ($r = 0.999$), and Me_2SnCl_2 ($r = 0.991$) in acetonitrile at 25°C.

The acceptor property of the tin is decreased by increasing the electron-releasing properties of the organo group and therefore lead to a decrease in formation of adducts. Increasing the number of chloride withdrawing groups increased acceptor properties of organotin chlorides. The phenyl group is more electron withdrawing than methyl and the trend of the adduct formation of R_2SnCl_2 compounds toward copper Schiff-base complexes is Ph > Me.

3.3.2. The donor properties of copper Schiff-base ligands.

The stability constant and the thermodynamic free energy for selected copper Schiff-base complexes toward organotin chlorides are collected in tables 1 and 2. Formation of adducts follow the sequence below:

$$\text{Cu(5-MeOSalen)} > \text{Cu(Salen)} > \text{Cu(5-BrSalen)} \gg \text{Cu(5-NO}_2\text{Salen)(no reaction)}.$$

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 $OCH_3 > H > Br$. Similar results have been reported previously for electrochemical properties of analogous Cu(II), Ni(II), V(IV), and Co(III) systems [23–25]. Also, the Ni(II) Schiff-base complexes as a ligand toward organotin chlorides show this property [8]. In fact, for selected Schiff bases, Hammett-type relationships were found between the log K values and σ_p, the para-substitute constant [26]. Such correlations are shown in figure 5. However, since the substituents at positions 5,5′ are para to the phenolic hydroxyl groups, Hammett-type correlations would indicate that the log K for the Schiff bases varies as a function of the acidity of the hydroxyl group through the ligand series.

To study the effect of position of substituent on the formation of adducts, Salen, 3-MeOSalen, 5-MeOSalen, Salophen, 3-MeOSalophen, and 5-MeOSalophen were examined. The results show the following trend in adduct formation between $PhSnCl_3$, Me_2SnCl_2, and copper Schiff-base complexes (table 1):

$$\text{Cu(3-MeOSalen)} > \text{Cu(5-MeOSalen)} > \text{Cu(Salen)}$$

and

$$\text{Cu(3-MeOSalophen} > \text{Cu(5-MeOSalophen)} > \text{Cu(Salophen)}.$$

From molecular structures of R_nSnCl_{4-n}·Metal(Schiff base) adducts [5], in the case of Cu(3-MeOSalen), the phenolic oxygen donors of N_2O_2 backbone and 3-MeO– groups participate in formation of the adducts (figure 2c), while in the other Schiff bases only the oxygen donor atoms of N_2O_2 backbone are bound to tin (figure 2a and 2b).

3.3.3. The steric effects of copper Schiff-base ligands. For finding the steric effects of the copper Schiff-base complexes we selected three Schiff bases with different diimine bridges (Salen, Salpn, and Salophen) with formation of adducts:

$$\text{Cu(Salpn)} > \text{Cu(Salen)} > \text{Cu(Salophen)}$$

Steric hindrance of the Schiff base decreases adduct formation. The geometry of the complexes from steric interactions of the bridges in Schiff bases affects the donor properties of the copper Schiff-base complexes.

Geometry of copper Schiff-base complexes is the most important factor governing the formation of adducts. The structure of these complexes increasingly distorted from planarity to almost tetrahedral geometry as the number of methylene units increase [27–29], allowing the metal greater freedom to change geometry. Therefore, distortion from square-planar geometry leads to a decrease in steric hindrance of acceptor and donor approach. Therefore, the Cu(Salpn) with three methylene groups is a better ligand toward R_nSnCl_{4-n}. Salen with two methylene groups has higher geometrical flexibility than Salophen [30]. Due to this, Cu(Salen) is better than Cu(Salophen) in adduct formation.

For Ph_2SnCl_2, the results show the following trend for adduct formation

$$\text{Cu(5-MeOSalen)} > \text{Cu(3-MeOSalen)} > \text{Cu(Salen)}$$

and

$$\text{Cu(5-MeOSalophen)} > \text{Cu(3-MeOSalophen)} > \text{Cu(Salophen)}$$

in contrast to the electronic effect of 3-MeO functional group [8–12]. It seems that the methoxy groups in 3-MeOSalen and 3-MeOSalophen have some steric effects that appear only when the steric on the acceptor is meaningful. By increasing the phenyl groups on the tin compounds, the size of these compounds increased making steric effects more important, while for Ph_2SnCl_2 and 3-MeOSalen, and 3-MeOSalophen, formation constants decrease because steric hindrance is as important.

3.3.4. The effect of temperature on the adduct formation. The formation constants of [Cu(Salen)], [Cu(Salpn)], and [Cu(Salophen] increase with increasing temperature.

For these complexes, the planar, tetrahedral equilibrium is reversibly temperature dependent and shifted toward tetrahedral with increasing temperature [31]. As previously

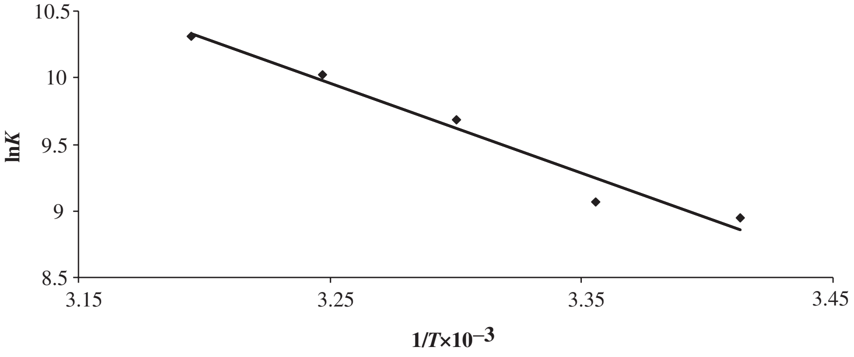

Figure 6. $\ln K$ *versus* $1/T$ for Cu(Salen) with $PhSnCl_3$.

described, distortion of the planar to tetrahedral geometry favored formation of adducts [29]. Therefore, formation constants were increased by increasing the temperature for [Cu(Salen)], [Cu(Salpn)], and [Cu(Salophen)] complexes as a ligand toward R_2SnCl_2.

3.4. *Thermodynamic parameters*

The $\ln K$ *versus* $1/T$ for Cu(Salen) titrated with $PhSnCl_3$ is shown in figure 6. The other systems are similar. The thermodynamic parameters ΔS°, ΔH°, and ΔG° for the adducts of Cu(Salen), Cu(Salpn), and Cu(Salophen) are collected in table 3.

3.4.1. Heat of formation. The value of ΔH° and its sign are dependent on heat of salvation and heat of formation of the adduct [32]. The heat of formation is exothermic while the liberation of solvent during adduct formation is endothermic. Changing geometry from square planar to tetrahedral by increasing the temperature has a positive effect on the heat of formation [27, 29, 33]. The overall contribution for solvation and change in geometry are dominant and the sign of the enthalpies are positive.

3.4.2. The entropy values. The ΔS° value and its sign also depend on two factors. For adduct formation the number of particles decreases and ΔS° is negative. The second factor is liberation of solvent from the solvation shells, which has a positive contribution to ΔS° [32]. Changes in geometry via increasing the temperature have a positive effect on the entropy [29, 33]. The overall contribution for solvation effect and the change in geometry dominate and the sign of entropies are positive.

4. Conclusions

By considering the formation constants and the ΔG° of the adduct formation for Cu(II) Schiff-base complexes with organotin(IV) chlorides, the following conclusions have been drawn:

1. The formation constant for a given donor changes according to the following trend for Cu(II) Schiff-bases due to electronic factors:

   Cu(5-MeOSalen) > Cu(Salen) > Cu(5-BrSalen)

   and

   Cu(3-MeOSalen) > Cu(5-MeOSalen) > Cu(Salen)

   and

   Cu(3-MeOSalophen) > Cu(5-MeOSalophen) > Cu(Salophen).

2. The formation constant for a given donor changes according to the following trend for Cu(II) Schiff-bases due to steric and electronic factors:

   Cu(5-MeOSalen) > Cu(3-MeOSalen) > Cu(Salen)

   and

   Cu(5-MeOSalophen) > Cu(3-MeOSalophen) > Cu(Salophen).

3. Formation constants for a given R_nSnCl_{4-n} acceptor toward the Cu(II) Schiff-base donors changes $PhSnCl_3 > Ph_2SnCl_2 > Me_2SnCl_2$.
4. The formation constants were increased by increasing temperature.

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References

[1] F. Marchetti, C. Pettinari, R. Pettinari, A. Cingolani, D. Leonesi, A. Lorenzotti. *Polyhedron*, **18**, 3041 (1999).
[2] E.N. Jacobsen. *Acc. Chem. Res.*, **33**, 421 (2000).
[3] D. Cunningham, J. Fitzgerald, M. Little. *J. Chem. Soc., Dalton Trans.*, 1 (1987).
[4] B. Clarke, N. Clarke, D. Cunningham. *J. Organomet. Chem.*, **559**, 55 (1998).
[5] D. Cunningham, B. Clarke, J.F. Gallagher, T. Higgins, P. McArdle, J. McGinley, Ni. Cholchuim. *J. Organomet. Chem.*, **469**, 33 (1994).
[6] L. Carbonaro, M. Isola, P.L. Pegna, L. Senatore, F. Marchetti. *Inorg. Chem.*, **38**, 5519 (1999).
[7] Y. Inada, K. Mochizuki, T. Tsuchiya, H. Tsuji, Sh. Funahashi. *Inorg. Chim. Acta*, **358**, 3009 (2005).
[8] M. Asadi, Kh. Aein Jamshid, A.H. Kianfar. *Inorg. Chim. Acta*, **360**, 1725 (2006).
[9] M. Asadi, Kh. Aein Jamshid, A.H. Kianfar. *Synth. React. Inorg., Met.-Org. Nano-Met. Chem.*, **37**, 77 (2007).
[10] M. Asadi, Kh. Aein Jamshid, A.H. Kianfar. *Transition Met. Chem.*, **32**, 822 (2007).
[11] M. Asadi, Kh. Aein Jamshid, A.H. Kianfar. *J. Coord. Chem.*, **61**, 1115 (2008).
[12] M. Asadi, Kh. Aein Jamshid, A.H. Kianfar. *J. Coord. Chem.*, accepted.
[13] M. Hariharan, F.L. Urbach. *Inorg. Chem.*, **8**, 556 (1969).

[14] E. Batley, D.P. Graddon. *Aust. J. Chem.*, **20**, 885 (1967).
[15] R.J. Tao, C.Z. Mei, S.Q. Zang, Q.L. Wang, J.Y. Niu, D.Z. Liao. *Inorg. Chim. Acta*, **357**, 1985 (2004).
[16] J.A.A. Ketelaar, C. Van De Stolpe, A. Coulsmit, W. Dzcubes. *Rec. Trav. Chim.*, **71**, 1104 (1952).
[17] D.J. Leggett. *Computational Methods for the Determination of Formation Constant*, Plenum Press, New York (1985).
[18] D.J. Leggett, S.L. Kelly, L.R. Shiue, Y.T. Wu. *Talanta*, **30**, 579 (1983).
[19] S.M. Grawford. *Spectrochim. Acta*, **19**, 255 (1963).
[20] S. Di Bella, I. Fragala, I. Ledoux, M. Diaz-Garcia, T. Marks. *J. Am. Chem. Soc.*, **119**, 9550 (1997).
[21] G.C. Percy, D.A. Thornton. *J. Inorg. Nucl. Chem.*, **35**, 2319 (1973).
[22] P. Gluvchinsky, G. Mockler. *Spectrochim. Acta*, **33A**, 1073 (1977).
[23] A.H. Sarvestani, A. Salimi, S. Mohebbi, R. Hallaj. *J. Chem. Res.*, **3**, 190 (2005).
[24] A.H. Sarvestani, S. Mohebbi. *J. Chem. Res.*, **4**, 257 (2006).
[25] E.G. Jager, K. Schuhmann, H. Gorls. *Inorg. Chim. Acta*, **255**, 295 (1997).
[26] A.J. Gordon, R.A. Ford. *The Chemist's Companion: A Handbook of Practical Data, Techniques, and References*, p. 145, Wiley, New York (1972).
[27] D. Cunningham, J.F. Gallagher, T. Higgins, P. McArdle, J. McGinley, M. O'Gara. *J. Chem. Soc., Dalton Trans.*, 2183 (1993).
[28] B. Clarke, D. Cunningham, J.F. Gallagher, T. Higgins, P. McArdle, J. McGinley, M. Ni Cholchuin. *J. Chem. Soc., Dalton Trans.*, 2473 (1994).
[29] M.K. Taylor, J. Reglinski, D. Wallace. *Polyhedron*, **23**, 3201 (2004).
[30] A. Giacomelli, T. Rotunno, L. Senatore. *Inorg. Chem.*, **24**, 1303 (1985).
[31] R. Knoch, H. Elias, H. Paulus. *Inorg. Chem.*, **34**, 4032 (1995).
[32] S. Ahrland. *Helv. Chim. Acta*, **50**, 306 (1967).
[33] D. Cunningham, M. Boyce, B. Clarke, J.F. Gallagher, T. Higgins, P. McArdle, J. McGinley, M. Ni Cholchuin, M. O'Gara. *J. Organomet. Chem.*, **498**, 241 (1995).