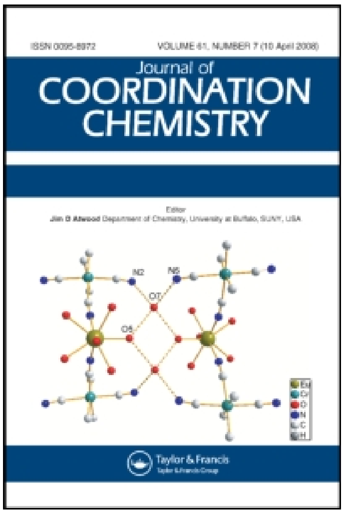

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Synthesis, characterization and thermal studies of dinuclear adducts of diorganotin(IV) dichlorides with nickel(II) Schiff-base complexes in chloroform

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The formation constants and free energies for the interaction of R_2SnCl_2 ($R =$ methyl, *n*-butyl, phenyl) as acceptors, with nickel Schiff-base complexes, ([NiL]) where $L =$ Salen [*N*,*N*′-*bis*(salicylaldehydo)ethylenediimine] (**1**), 7,7′-Me_2Salen [*N*,*N*′-*bis*(2-hydroxyacetophenone) ethylenediimine] (**2**), Salpn [*N*,*N*′-*bis*(salicylaldehydo)-1,3-propanediimine] (**3**), Salophen [*N*,*N*′-*bis*(salicylaldehydo)-1,2-phenylenediimine] (**4**) as donors and also the interaction of Ph_2SnCl_2 with [NiL′], where $L' =$ [5-methoxysalen, *N*,*N*′-*bis*(5-methoxysalicylidene)ethylenediimine] (**5**), [5-methoxysalophen, *N*,*N*′-*bis*(5-methoxysalicylidene)-1,2-phenylenediimine] (**6**) and [5-chlorosalen, *N*,*N*′-*bis*(5-chlorosalicylidene)ethylenediimine] (**7**) in chloroform have been studied. The complexes and adducts have been characterized by ^1H, ^{13}C and ^{119}Sn NMR, IR and electronic spectroscopy and elemental microanalysis. Formation constants and thermodynamic free energies were measured using UV–Vis spectrophotometric titration for 1:1 adducts. Data refinement was carried out with SQUAD 84 program. The trend of adduct formation for the nickel Schiff-base complexes with a given tin acceptor decreases:

$$\text{Salpn} > 7,7'\text{-Me}_2\text{Salen} > 5\text{-MeOSalen} > \text{Salen} > 5\text{-MeOSalophen} > \text{Salophen} > 5\text{-ClSalen}$$

The trend for R_2SnCl_2 acceptors toward a given nickel Schiff-base complex is:

$$\text{Me} > \text{Ph} > n\text{-Bu}$$

Keywords: Nickel; Schiff base; Diorganotin dichloride; Formation constants; Adduct formation; Thermodynamic

1. Introduction

Schiff-base complexes have remained important due to their simple synthesis, versatility and diverse applications [1]. Nickel(II) complexes with N_2O_2 Schiff-base ligands derived from salicylaldehyde have been used as homogeneous catalysts [2] for oxidation,

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aziridine formation, epoxide opening and cycloaddition, both asymmetric and non-stereoselective [3].

Tetradentate Schiff-base metal complexes with an N_2O_2 donor atom set can be bidentate chelating ligands for metal(I, II) cations producing binuclear complexes with different Lewis acid–base properties, promoting coordination and activation of small molecules [4, 5].

Synthesis and structural characterization of several metal(II) salen complexes as bidentate donors to tin(IV) compounds have been investigated [6, 7], but very little is known of their formation constants in solution. Alkali and alkaline earth ions in acetonitrile solution were found to form 1:1 adducts with transition metal Schiff-base complexes [8, 9].

In this study the formation constants and free energies of Ni(Salen), Ni(7,7′-Me_2Salen), Ni(Salpn) and Ni(Salophen) as donor ligands with Me_2SnCl_2, Bu_2SnCl_2 and Ph_2SnCl_2 as acceptors, and also those for Ni(5-MeOSalen), Ni(5-MeOSalophen), Ni(5-ClSalen) with Ph_2SnCl_2 in chloroform, have been examined (see figure 1). By comparing the spectral and thermodynamic properties of the complexes, we investigate the effects of different electronic and steric situations.

2. Experimental

2.1. *Apparatus and reagents*

UV–Vis measurements were carried out in a JASCO V-530 UV–Vis spectrophotometer equipped with a LAUDA ecoline RE 104 thermostat. The ^{1}H (250 MHz, $CDCl_3$, TMS) and ^{13}C NMR (62.9 MHz, $CDCl_3$, TMS) spectra were recorded by a Bruker Avance DPX 250 MHz spectrometer and ^{119}Sn NMR (149.2 MHz, $CDCl_3$, Me_4Sn) spectra were recorded by a Bruker Avance DPX 400 MHz spectrometer. IR spectra were recorded on a Shimadzu FTIR 8300 infrared spectrophotometer. Microanalyses were carried out on a CHN ThermoFinnigan Flash EA1112 instrument. Melting points were determined on a BUCHI 535.

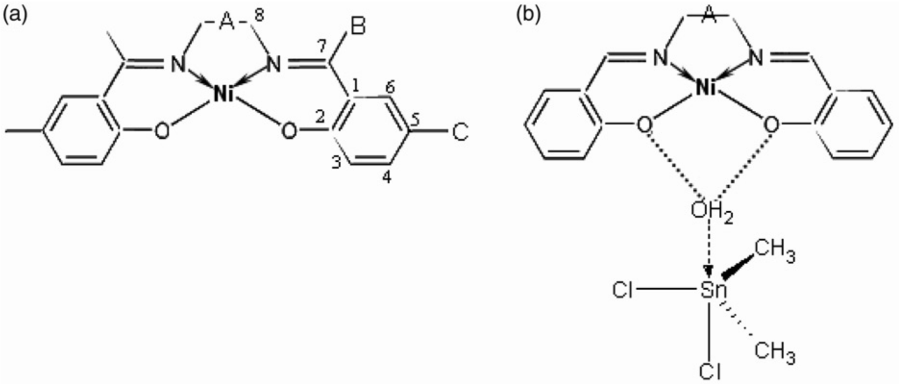
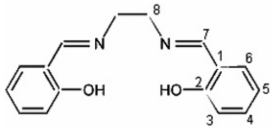


Figure 1. Structural representation of (a) the nickel Schiff-base complexes and (b) their adducts, $A = -(CH_2CH_2)-$, $-(CH_2CH_2CH_2)-$ and $-o-C_6H_4-$; $B = H$ and Me, $C =$ MeO, H and Cl.

Salicylaldehyde, 2-hydroxy-acetophenone, 5-methoxysalicylaldehyde, 5-chlorosalicylaldehyde, *o*-phenylenediamine, 1,3-propanediamine, 1,2-ethylenediamine, methanol, ethanol, chloroform, dibutyltin dichloride and nickel acetate tetrahydrate were purchased from Merck, Fluka or Aldrich and used without further purification. Dimethyltin dichloride and diphenyltin dichloride were purchased from Merck and purified before using.

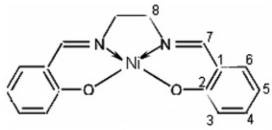
2.2. *Synthesis of Schiff bases and their nickel complexes*

2.2.1. *N*,*N*′-Ethylene bis(salicylideneamine), (SalenH$_2$) A. The ligand *N*,*N*′-ethylene bis(salicylideneamine), $C_{16}H_{16}N_2O_2$ (SalenH$_2$) **A**, was prepared according to previously published methods [10]. A solution of the salicylaldehyde (5 mmol, 0.53 cm^3) in 25 cm^3 of dried ethanol was added to an ethanolic solution of the ethylenediamine (2.5 mmol, 0.17 cm^3), the reaction mixture was refluxed for 30 min and then the mixture was cooled. **A** separated as yellow needles and was recrystallized twice from methanol (0.57 g, 85%, m.p. 128.9°C). (Found: C, 71.87; H, 6.23; N, 10.67. $C_{16}H_{16}N_2O_2$ requires C, 71.62; H, 6.01; N, 10.44%); δ_H (250 MHz; CDCl$_3$; Me$_4$Si) 13.19 (2 H, s, OH), 8.67 (2 H, s, C7, C7′), 6.82–7.30 (8 H, m, C1–C6, C1′–C6′), 4.01 (4 H, s, C8, C8′); δ_C (62.9 MHz; CDCl$_3$; Me$_4$Si) 166.78 (4 C, d, C2, C7), 58.79 (2 C, singlet, C8), 117.34, 118.54, 131.90 and 133.18 (8 C, d, aromatic C); ν/cm^{-1} 1635 (C=N), 1458–1578 (C=C), 1284 (C–O); λ_{max}(CHCl$_3$)/nm 318, 408.



Nickel Schiff-base complexes were prepared using a method described in the literature by Batley and Graddon [11].

2.2.2. (*N*,*N*′-bis(Salicyliden)-ethylenediiminato)nickel(II), Ni(Salen) 1. A solution of the nickel acetate tetrahydrate (2 mmol, 0.50 g) in 50 cm^3 of ethanol was added to 50 cm^3 of an ethanolic solution containing SalenH$_2$, **A** (2 mmol) and the mixture was refluxed for 2 h; after slowly cooling, the product was formed. The product was filtered, washed with cold ethanol and dried in a dessicator over phosphorous(V) oxide. **1** separated as brown needles and was recrystallized twice from methanol (0.52 g, 80%, m.p. over 300°C). (Found: C, 58.59; H, 3.96; N, 8.93. $C_{16}H_{14}N_2O_2Ni$ requires C, 58.26; H, 4.28; N, 8.49%); δ_H (250 MHz; CDCl$_3$; Me$_4$Si) 7.67 (2 H, s, C7, C7′), 6.48–7.40 (8 H, m, C1–C6, C1′–C6′), 3.44 (4 H, s, C8, C8′); δ_C (62.9 MHz; CDCl$_3$; Me$_4$Si) 166.49 (2 C, s, C2), 132.37 (2 C, s, C7) 59.75 (2 C, singlet, C8), 116.93, 118.66 and 131.46 (8 C, d, aromatic C); ν/cm^{-1} 1624 (C=N), 1419–1537 (C=C), 1250 (C–O); λ_{max} (CHCl$_3$)/nm 330, 414.

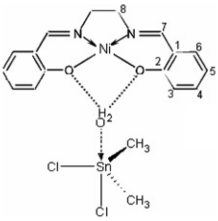


The other nickel Schiff-base complexes, **2–7**, were synthesized using the above procedure. The characterization data of the nickel Schiff-base complexes are collected in tables 1–4.

2.3. *Synthesis of adducts of diorganotin dichloride with nickel Schiff-base complexes*

The adducts were prepared using a method described by Cunningham [12].

2.3.1. Ni(Salen)•Me_2SnCl_2•H_2O (1a). A solution of **1** (1.625 g, 5 mmol) in 25 cm^3 of chloroform was added to 25 cm^3 of a chloroformic solution of dimethyltin dichloride (1.098 g, 5 mmol) and the mixture stirred for 4 h. Red crystals of Me_2SnCl_2·[Ni(Salen)]·H_2O were filtered, recrystallized with chloroform and dried in a dessicator (1.828 g, 65%, m.p. over 300°C). (Found: C, 38.12; H, 4.29; N, 5.23. $C_{18}H_{22}N_2O_3Cl_2NiSn$ requires C, 38.42; H, 3.94; N, 4.98%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 7.50 (2 H, s, C7, C7′), 6.51–7.26 (8 H, m, C1–C6, C1′–C6′), 3.49 (4 H, s, C8, C8′), 1.20 (6 H, s, $^{2}J(^{1}H{-}^{119}Sn)$ 68, Me_2Sn); δ_C (62.9 MHz; $CDCl_3$; Me_4Si) 162.09 (2 C, s, C2), 137.03 (2 C, s, C7), 58.45 (2 C, singlet, C8), 115.14, 121.20, 132.47 and 133.83 (8 C, d, aromatic C), 13.21 (2 C, s, $^{1}J(^{13}C{-}^{119}Sn)$ 695.5, Me_2Sn); C–Sn–C (θ°), 137.8°; δ_{Sn} (149.2 MHz; $CDCl_3$; Me_4Sn) + 137.36 (1 Sn, s); ν/cm^{-1} 1649 (C=N), 1450–1546 (C=C), 1280 (C–O); λ_{max} ($CHCl_3$)/nm < 300 (π–π*), 392 (MLCT).



2.3.2. Ni(Salen)•$(n\text{-}Bu)_2SnCl_2$•H_2O (1b). A solution of **1** (1.625 g, 5 mmol) in 25 cm^3 of chloroform was added to 25 cm^3 of a chloroformic solution of dibutyltin dichloride (1.519 g, 5 mmol) and the mixture stirred for 4 h. Brown crystals of $(n\text{-}Bu)_2SnCl_2$·[Ni(Salen)]·H_2O were filtered, recrystallized with chloroform and dried in a dessicator (1.940 g, 60%, m.p. over 300°C). (Found: C, 44.19; H, 5.46; N, 4.71. $C_{24}H_{34}N_2O_3Cl_2NiSn$ requires C, 44.56; H, 5.30; N, 4.33%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 7.36 (2 H, s, C7, C7′), 6.49–7.22 (8 H, m, C1–C6, C1′–C6′), 3.44 (4 H, s, C8, C8′), 0.93–1.84 (18 H, m, Bu_2Sn); δ_{Sn} (149.2 MHz; $CDCl_3$; Me_4Sn) + 7.09 (1 Sn, s); ν/cm^{-1} 1620 (C=N), 1450–1535 (C=C), 1203 (C–O); λ_{max} ($CHCl_3$)/nm < 300 (the π–π* band overlaps with chloroform bands), 392 (MLCT).

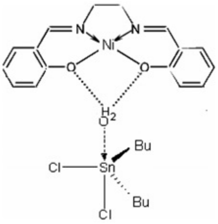


Table 1. Analytical data of the Schiff-base complexes.

Compound	Found (Calcd[a]) (%)		
	C	H	N
Ni(Salen) (**1**)	58.59 (58.26)	3.96 (4.28)	8.93 (8.49)
Ni(Me_2Salen) (**2**)	60.98 (61.24)	5.36(5.14)	8.24 (8.63)
Ni(Salpn) (**3**)	59.91 (60.23)	4.99 (4.76)	8.63 (8.26)
Ni(Salophen) (**4**)	64.92 (64.40)	4.01 (3.78)	7.96 (7.51)
Ni(5-MeOSalen) (**5**)	56.36 (56.15)	4.24 (4.71)	7.45 (7.28)
Ni(5-MeOSalophen) (**6**)	61.43 (61.01)	3.75 (4.19)	6.81 (6.47)
Ni(5-ClSalen) (**7**)	49.25 (48.79)	3.19 (3.07)	7.46 (7.11)

[a] The data was calculated using Microsoft Excel 2003.

Table 2. UV–Vis bands λ_{max}[CH_3Cl(nm)] of the nickel Schiff-base complexes.

Complex	$\lambda(\pi–\pi^*)$	λ(MLCT)
1	330	412
2	334	410
3	<300[a]	354
4	380	478
5	334	438
6	388	514
7	330	424

[a] The $\pi–\pi^*$ band has overlap with chloroform bands.

Table 3. ^{1}H-NMR (250 MHz, $CDCl_3$, room temperature, TMS, δ, ppm) spectroscopic data[a] of the compounds.

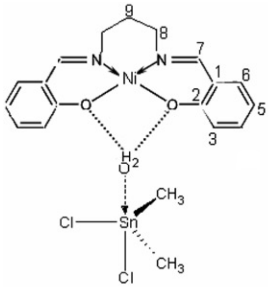
Complex	C7, C7′ (2H, s)	C1–C6, C1′–C6′ (8H, m)	C8, C8′ (4H, s)
1	7.67	6.48–7.40	3.44
2	2.21[b]	6.46–7.54	3.48
3	8.39	6.79–7.29	3.55
4	8.28	6.67–7.75	–
5	7.46	6.43–7.24	3.45
6	8.60	6.79–7.56	–
7	7.44	6.94–7.16	3.45

[a] Chemical shifts in ppm. s, singlet; m, multiplet.
[b] The protons of C(Me)=N instead of CH=N.

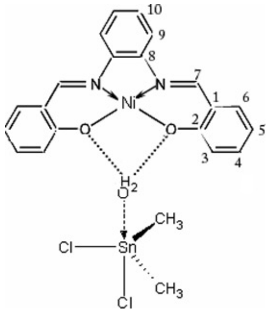
Table 4. IR characterization (ν in cm^{-1}) of the nickel Schiff-base complexes.

Complex	ν(C=N)	ν(C=C)	(C–O)
A	1635	1458–1578	1284
1	1624	1419–1537	1250
2	1605	1442–1582	1246
3	1633	1469–1597	1250
4	1605	1491–1576	1340
5	1612	1442–1527	1226
6	1605	1462–1581	1365
7	1624	1460–1529	1313

2.3.3. Ni(Salpn)•Me_2SnCl_2•H_2O (3a). A solution of **3** (1.695 g, 5 mmol) in 25 cm^3 of chloroform was added to 25 cm^3 of a chloroformic solution of dimethyltin dichloride (1.098 g, 5 mmol) and stirred for 4 h. Green crystals of $Me_2SnCl_2 \cdot [Ni(Salpn)] \cdot H_2O$ were filtered, recrystallized with chloroform and dried in a dessicator (1.297 g, 45%, m.p. over 300°C). (Found: C, 39.87; H, 3.79; N, 5.12. $C_{19}H_{24}N_2O_3Cl_2NiSn$ requires C, 39.57; H, 4.19; N, 4.86%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 8.28 (2 H, s, C7, C7′), 6.86–7.42 (8 H, m, C1–C6, C1′–C6′), 3.64 (4 H, s, C8, C8′), 1.21 (6 H, s, $^2J(^1H–^{119}Sn)$ 67, Me_2Sn); δ_C (62.9 MHz; $CDCl_3$; Me_4Si) 161.88 (2 C, s, C2), 134.82 (2 C, s, C7), 59.24 (2 C, singlet, C8), 28.02 (1 C, singlet, C9), 114.93, 121.25 and 133.46 (8 C, d, aromatic C), 13.61 (2 C, s, $^1J(^{13}C–^{119}Sn)$ 699.2, Me_2Sn); C–Sn–C (θ°), 138.1°; δ_{Sn} (149.2 MHz; $CDCl_3$; Me_4Sn) + 101.76 (1 Sn, s); ν/cm^{-1} 1659 (C=N), 1470–1600 (C=C), 1283 (C–O); λ_{max} ($CHCl_3$)/nm < 300 (the π–π* band overlaps with chloroform bands), 338 (MLCT).



2.3.4. Ni(Salophen) • Me_2SnCl_2 • H_2O (4a). A solution of **4** (1.865 g, 5 mmol) in 25 cm^3 of chloroform was added to 25 cm^3 of a chloroformic solution of dimethyltin dichloride (1.098 g, 5 mmol) and mixture stirred for 4 h. Red crystals of $Me_2SnCl_2 \cdot [Ni(Salophen)] \cdot H_2O$ were filtered, recrystallized with chloroform and dried in a dessicator (1.374 g, 45%, m.p. over 300°C). (Found: C, 43.16; H, 3.85; N, 4.90. $C_{22}H_{24}N_2O_3Cl_2NiSn$ requires C, 43.12; H, 3.95; N, 4.57%); δ_H (250 MHz; $CDCl_3$; Me_4Si) 8.43 (2 H, s, C7, C7′), 6.65–7.75 (8 H, m, C1–C6, C1′–C6′), 3.49 (4 H, s, C8-10, 8′-10′), 1.21 (6 H, s, $^2J(^1H–^{119}Sn)$ 61, Me_2Sn); δ_C (62.9 MHz; $CDCl_3$; Me_4Si) 160.95 (2 C, s, C2), 137.18 (2 C, s, C7) 124.27 (6 C, singlet, bridge phenyl ring), 114.69, 121.75, 132.09 and 133.53 (8 C, d, aromatic C), 18.76 (2 C, s, $^1J(^{13}C–^{119}Sn)$ 602.3, Me_2Sn); C–Sn–C (θ°), 129.6°; δ_{Sn} (149.2 MHz; $CDCl_3$; Me_4Sn) + 139.79 (1 Sn, s); ν/cm^{-1} 1632 (C=N), 1430–1579 (C=C), 1331 (C–O); λ_{max} ($CHCl_3$)/nm 372 (π–π*), 446 (MLCT).



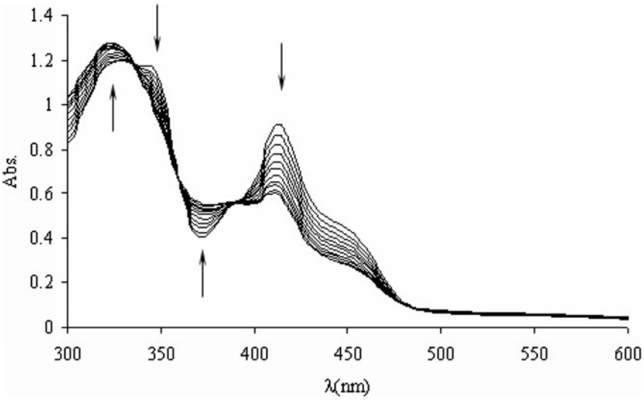


Figure 2. Spectrophotometric titration of **1** [1.29×10^{-4} M] with Ph_2SnCl_2 [1.96×10^{-2}–1.96×10^{-1} M] in chloroform at 5°C.

2.4. *Equilibrium measurements*

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

$$\mathrm{Ni(L)} + \mathrm{R_2SnCl_2} \rightleftharpoons \mathrm{R_2SnCl_2Ni(L) \cdot H_2O} \tag{1}$$

where $L =$ Salen, Me_2Salen, Salpn, Salophen, 5-MeOSalen, 5-MeOSalophen, 5-ClSalen and $R =$ methyl, *n*-butyl, phenyl.

UV–Vis measurements were carried out by spectrophotometric titration at $T = 5$, 15, 25 and 35 (±0.1)°C. In a typical measurement, 2.5 mL solution of [NiL] (10^{-4} M) in chloroform was titrated with R_2SnCl_2 (10^{-4}–10^{-1} M). The acceptor concentrations were varied from one-to-ten fold excess. UV–Vis spectra were recorded in the range 300–700 nm 5 min after each addition. The absorption measurements were carried out at various wavelengths in the 310 to 530 nm region, where the difference in absorption between the substrate and the product was largest after the equilibrium was attained. As an example, the variation of the electronic spectra for **1**, titrated with diphenyltin dichloride in chloroform, are shown in figure 2. The isosbestic points suggest there are only two species in equilibrium. The same is valid for other systems.

3. Results and discussion

The reported X-ray diffraction analysis [6, 7] of the adducts of nickel Schiff-base complexes with diorganotin dianions (similar to our synthesized adducts of **1a**, **1b**, **3a** and **4a**) show that the square-planar or distorted tetrahedral geometry of nickel in the adducts in non polar or weakly polar solvent such as chloroform is the same as its complexes. The geometry of the tin changed from tetrahedral in R_2SnCl_2 to trigonal bipyramidal in the adducts (see figure 1). Microanalyses and the C–Sn–C angle, calculated using Lockhart equation, are in good agreement with previous investigations [6, 7].

3.1. *Spectral characterization*

3.1.1. Electronic spectra. All nickel Schiff-base complexes show a relatively intense band in the 310–400 nm region, involving π–π^* transition [13], and a broader band between 380–530 nm, involving n–π^* transition [14]. Upon interaction with diorganotin dichlorides, a new MLCT band appeared (see figure 2). The clear isosbestic points in figure 2 represent the adduct formation in solution. Table 2 gives the original peaks of the nickel Schiff-base complexes.

3.1.2. NMR spectra. ^{1}H NMR spectra of the nickel Schiff-base complexes are collected in table 4. The ^{13}C and ^{119}Sn NMR spectra were collected for **1a** (Supplemental Material), **1b**, **3a** and **4a** in section 2.2. and 2.3

In the ^{1}H NMR, upon the complexation of Schiff base with nickel ion, the phenolic O-H disappeared and the other resonances shifted to higher field. The adducts with diorganotin dichlorides are identified by appearance of Me_2Sn resonances in the region $\delta = 1.07$–1.48 ppm, $\delta = 7.37$–7.98 ppm for Ph_2SnCl_2 and $\delta = 0.68$–1.98 ppm for $(n\text{-Bu})_2SnCl_2$. In the case of Ph_2SnCl_2, the signal of phenyl interfered with signals of aldimine and aromatic protons. Adduct formation causes a shift to lower field of the aldimine protons.

Tin satellites were clearly observed in ^{1}H and ^{13}C NMR spectra of the tin adducts. The $^1J(^{119}\text{Sn}–^{13}\text{C})$ and $^2J(^{119}\text{Sn}–^1\text{H})$ coupling constant values of the adducts are collected in table 4. The Me–Sn–Me angle, θ, of the adducts, calculated from the ^{13}C NMR spectra using Lockhart equation (2) [15], are in good agreement with Cunningham *et al.* [5–8].

$$|^1J| = 11.4(\theta^\circ) - 875 \tag{2}$$

In ^{119}Sn NMR spectra of the adducts a sharp singlet for Me_2Sn appeared at +137, +7, +102 and +140 ppm for **1a**, **1b**, **3a** and **4a**, respectively.

3.1.3. IR spectra. The strong IR band between 1605 cm^{-1} and 1633 cm^{-1} is assigned to the C=N characteristic for Schiff bases. The ring skeletal vibrations (C=C) of Schiff bases were in the region 1419–1597 cm^{-1}. The phenolic C–O stretching vibrations appeared at 1246–1365 cm^{-1} in the Schiff-base complexes. These observations are in good agreement with previous investigations [16, 17].

In the adducts, C=N, ring skeletal vibrations (C=C) and phenolic C–O bands shift to higher frequencies (30–50 cm^{-1}).

3.2. *Microanalyses*

Table 1 shows that elemental analyses are in good agreement with 1:1 composition of the adducts of nickel complexes with dimethyltin(IV) dichlorides.

3.3. *Formation constants and free energy calculations*

The average formation constants of the adducts were calculated in the selected range of spectra by using the well-known Ketelaar equation (3)[18] and SQUAD 84 program [19, 20].

$$(C_A^\circ C_D^\circ)/(A - A_A^\circ - A_D^\circ) = (1/(\varepsilon_C - \varepsilon_A - \varepsilon_D))[(1/K) + (C_A^\circ + C_D^\circ)] \tag{3}$$

where C_A° and C_D° are the initial concentrations ($\mathrm{mol} \times \mathrm{dm}^{-3}$) of the acceptor and the 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 the pure donor in solution of concentration C_A° and C_D°; ε_C, ε_A and ε_D are the molar absorption coefficients ($\mathrm{dm}^3 \times \mathrm{mol}^{-1} \times \mathrm{cm}^{-1}$) 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. The absorption measurements were monitored at various wavelengths from 320 to 480 nm, where the difference in absorption between the Ni(II) substrate and the product was the largest after equilibrium was attained. Variation of the electronic spectra for **1**, titrated with diphenyltin dichloride in chloroform, is shown in figure 2. The isosbestic points suggest only two species in equilibrium. A plot of $C_A^\circ \times C_D^\circ/(A - A_A^\circ - A_D^\circ)$ *versus* $C_A^\circ + C_D^\circ$ should produce a straight line if only a 1:1 complex is formed. The formation constants of the studied nickel(II) Schiff-base adducts were calculated from the ratio of the slope to the intercept by least squares method using Microsoft Excel 2003 computer software. The K measurements were repeated at least twice and were reproducible. Linear plots for **1** titrated with Me_2SnCl_2 at various wavelengths at 25°C in chloroform are shown in figure 3, which signify that only a 1:1 adduct is formed.

The obtained values for 1:1 adducts were compared using both methods (Ketelaar and SQUAD 84) showing no significant incoherence. SQUAD is a program with the capability of refining the formation constants of a general complex $M_mM_lH_kL_nL_q$, where $m, l, n, q \geq 0$ and k are 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 (4):

$$U = \sum_{\mathrm{I}}^{\mathrm{I}} \sum_{\mathrm{I}}^{\mathrm{NW}} (A_{i,k}^{\mathrm{Calcd}} - A_{i,k}^{\mathrm{obs}})^2 \tag{4}$$

where the $A_{i,k}$ 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.

Log K_{av} and K_{av} values for Ni(Salen) with dimethyltin dichloride in chloroform solvent at 25°C, obtained by using Ketelaar equation and SQUAD 84 program, are 1.73 (53.75) and 1.75 (56.28), respectively (stability constants values in parenthesis).

The formation constants and the free energies are collected in table 5 and Supplemental Material.

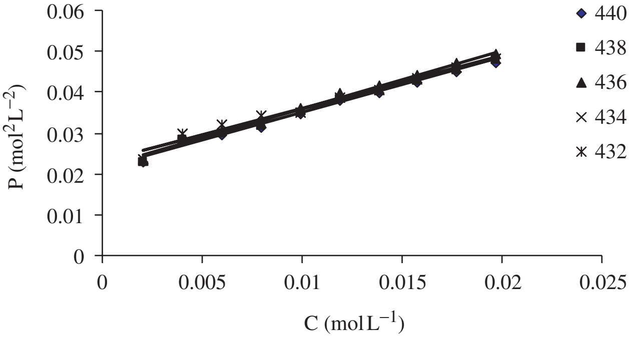


Figure 3. Ketelaar plots of variable P *vs*. C for **5** [1.25×10^{-4} M] with Ph_2SnCl_2 [1.96×10^{-3}–1.96×10^{-2} M] in chloroform at various wavelengths (nm^{-1}) at 25°C, where $P = (C_A^\circ C_D^\circ)/(A - A_A^\circ - A_D^\circ)$ and $C = (C_A^\circ + C_D^\circ)$.

Table 5. The formation constants, K_{av} ($L\,mol^{-1}$), for nickel Schiff-base [NiL] complexes with diorganotin dichlorides in chloroform.

	L	5°C	15°C	25°C	35°C
Me_2SnCl_2	Salpn	$(1.60 \pm 0.12) \times 10^4$	$(1.48 \pm 0.09) \times 10^4$	$(1.26 \pm 0.05) \times 10^4$	$(7.88 \pm 0.64) \times 10^3$
	Me_2Salen	$(4.13 \pm 0.20) \times 10^3$	$(3.72 \pm 0.19) \times 10^3$	$(2.26 \pm 0.10) \times 10^3$	$(1.97 \pm 0.07) \times 10^3$
	Salen	$(4.18 \pm 0.10) \times 10^1$	$(5.26 \pm 0.13) \times 10^1$	$(5.37 \pm 0.16) \times 10^1$	$(6.04 \pm 0.13) \times 10^1$
	Salophen	$(1.20 \pm 0.09) \times 10^1$	$(2.21 \pm 0.13) \times 10^1$	$(2.26 \pm 0.14) \times 10^1$	$(2.82 \pm 0.15) \times 10^1$
Ph_2SnCl_2	Salpn	$(2.50 \pm 0.15) \times 10^3$	$(2.47 \pm 0.15) \times 10^3$	$(2.47 \pm 0.16) \times 10^3$	$(2.46 \pm 0.13) \times 10^3$
	Me_2Salen	$(7.47 \pm 0.46) \times 10^1$	$(5.36 \pm 0.26) \times 10^1$	$(3.08 \pm 0.18) \times 10^1$	$(2.81 \pm 0.19) \times 10^1$
	5-MeOSalen	$(3.93 \pm 0.20) \times 10^1$	$(3.61 \pm 0.08) \times 10^1$	$(3.59 \pm 0.07) \times 10^1$	$(2.62 \pm 0.08) \times 10^1$
	Salen	$(1.77 \pm 0.06) \times 10^1$	$(1.87 \pm 0.06) \times 10^1$	$(2.29 \pm 0.01) \times 10^1$	$(2.51 \pm 0.13) \times 10^1$
	5-MeOSalophen	$(1.24 \pm 0.07) \times 10^1$	$(9.62 \pm 0.41) \times 10^0$	$(8.47 \pm 0.35) \times 10^0$	$(8.06 \pm 0.34) \times 10^0$
	Salophen	$(8.16 \pm 0.39) \times 10^0$	$(8.54 \pm 0.45) \times 10^0$	$(8.65 \pm 0.42) \times 10^0$	$(9.33 \pm 0.46) \times 10^0$
	5-ClSalen	$(1.07 \pm 0.06) \times 10^1$	$(8.60 \pm 0.46) \times 10^0$	$(9.43 \pm 0.52) \times 10^0$	$(7.48 \pm 0.53) \times 10^0$
$(n\text{-Bu})_2SnCl_2$	Salpn	$(1.04 \pm 0.16) \times 10^4$	$(8.52 \pm 0.60) \times 10^3$	$(6.62 \pm 0.31) \times 10^3$	$(4.69 \pm 0.18) \times 10^3$
	Me_2Salen	$(6.83 \pm 0.69) \times 10^1$	$(5.66 \pm 0.29) \times 10^1$	$(4.11 \pm 0.20) \times 10^1$	$(3.39 \pm 0.10) \times 10^1$
	Salen	$(5.53 \pm 0.26) \times 10^0$	$(6.34 \pm 0.28) \times 10^0$	$(6.60 \pm 0.32) \times 10^0$	$(7.61 \pm 0.44) \times 10^0$
	Salophen	$(4.42 \pm 0.22) \times 10^0$	$(4.48 \pm 0.22) \times 10^0$	$(4.52 \pm 0.22) \times 10^0$	$(4.68 \pm 0.25) \times 10^0$

3.4. *Formation constants*

The synthesis and structural characterization of nickel Schiff-base complexes as a ligand with tin and organotin halides were widely investigated [6, 7], but there is no evidence about the interaction of these compounds in solution. To study the effects of electronic and steric parameters of donors and acceptors on the formation constants and the free energy, the interaction of the nickel Schiff-base complexes as donors with R_2SnCl_2 as acceptors show that the formation constants are related to the type of Schiff base, organo groups on R_2SnCl_2 and the temperature.

3.4.1. The acceptor properties of diorganotin dichlorides. We examined dimethyltin, dibutyltin and diphenyltin dichloride. Acceptor capability of the tin is decreased by electron-releasing properties of the organo group; alkyl groups decrease the acceptor capability while aryl groups have a reverse effect. The greater the bulkiness of the organo group decreases formation of adducts. The trend of the adduct formation of R_2SnCl_2 compounds toward nickel Schiff-base complexes is:

$$\mathrm{Me} > \mathrm{Ph} > n\text{-Bu}$$

3.4.2. The donor properties of nickel Schiff-base ligands. The stability constants in table 5 and Supplemental Material show the sequence:

$$\mathrm{Ni(Salpn)} > \mathrm{Ni(7,7'\text{-}Me_2Salen)} > \mathrm{Ni(Salen)} > \mathrm{Ni(Salophen)}$$

For studying the electronic effect of Schiff bases, the three Schiff bases Salen, Me_2Salen and Salophen were selected. The methyl groups in Me_2Salen make **2** a better donor than **1**; the Salophen Schiff base with a π-system make **4** a poor donor, so adduct formation between **4** and R_2SnCl_2 are lowest.

The nickel Schiff-base complexes have coplanar geometry [6, 7], increasingly distorted from planarity to almost tetrahedral geometry as the number of methylene units increase [21]. Distortion from square-planar geometry leads to a decrease in steric hindrance in the acceptor and the donor approaching. Therefore, **3** is a better ligand toward R_2SnCl_2 and **1** donates better than **4** in the adduct formation [22].

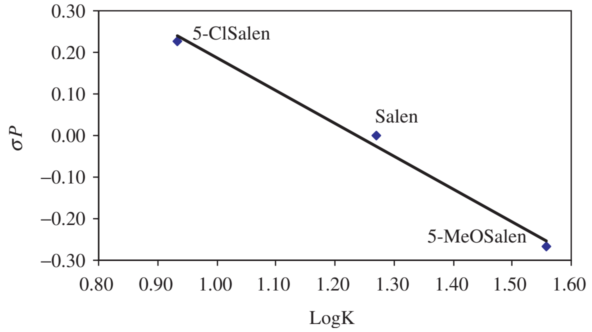


Figure 4. Linear correlation between the para substituted constants, σP, and $\log K$ for nickel substituted salen complexes with Ph_2SnCl_2 in chloroform at 15°C.

Electronic effects of the substituents are shown by 5-MeOSalen, 5-MeOSalophen, Salen and 5-ClSalen.

$$\text{Ni(5-MeOSalen)} > \text{Ni(Salen)} > \text{Ni(5-MeOSalophen)} > \text{Ni(5-ClSalen)}$$

Thus, the stability constants decrease according to the sequence $OCH_3 > H > Cl$; similar results have been reported for electrochemical properties of analogous Cu(II), Ni(II) and Co(III) systems [23–25]. In fact, Hammett-type relationships were found between the log K values and σ_p, the *para*-substituent constant [26], figure 4.

In the case of **6** and **7**, the 5-MeO electron releasing groups and the *o*-phenylenediamine electron withdrawing group made **6** a better donor than **7**.

3.5. *Effect of temperature on adduct formation*

The formation constants were carried out at various temperatures. Because of bond formation, by increasing the temperature, the formation constants decreased.

Complexes **1** and **4** show a reverse trend, probably because the geometry changes to tetrahedral with increasing temperature. In the case of these two complexes, the equilibrium of the planar and tetrahedral is reversibly temperature dependent and shifted toward the tetrahedral isomer with increasing temperature [27]. We recorded the spectra of **1** and **4** in chloroform in the temperature range $T = 5$–55°C. The typical "planar" bands of **1** and **4** at 414 and 482 nm, respectively, decrease with increasing temperature; distortion of planar to tetrahedral geometry favors formation of adducts.

4. Conclusions

By considering the formation constants of adduct formation for Ni(II) Schiff-base complexes as donor and diorganotin(IV) dichlorides as acceptor, the following conclusions have been drawn:

(1) The formation constant for nickel(II) Schiff-base complexes toward a given diorganotin dichloride, due to the geometry, steric and electronic factors, changes according to the following trend:

$$\text{Salpn} > 7,7'\text{-Me}_2\text{Salen} > \text{5-MeOSalen} > \text{Salen} > \text{5-MeOSalophen} > \text{Salophen} > \text{5-ClSalen}$$

(2) The formation constants for a given R_2SnCl_2 acceptor toward the Schiff-base donor changes according to the following trend:

$$Me > Ph > n\text{-}Bu$$

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