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Synthesis, Mechanism and Kinetic Studies of Cobalt(II) Schiff base Complexes with Organotin(IV) Chlorides

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ABSTRACT

The kinetics and mechanism of the adduct formation of diorganotin(IV)dichlorides (R_2SnCl_2) where R=Ph, Me, Bu and triphenyltin(IV)chloride with Co(II) tetraaza Schiff base complexes such as: [Co(ampen)] {[N,N'-ethylenebis-(*o*-amino-α-phenylbenzylideneiminato)cobalt(II)]}, [Co(campen)] {[N,N'-ethylenebis-(5-chloro-*o*-amino-α-phenylbenzylideneiminato)cobalt(II)]} and [Co(amaen)] {[N,N'-ethylenebis-(*o*-amino-α-methylbenzylideneiminato)cobalt(II)]}, [Co(appn)] {[N,N'-1,2-propylenebis-(o-amino-α-phenylbenzylideneiminato)cobalt(II)]}, [Co(cappn)]{[N,N'-1,2-proylenebis-(5-chloro-o-amino-α-phenylbenzylideneiminato-)cobalt(II)]} were studied spectrophotometrically. The kinetic parameters and the rate constant values show the acceptor tendency trend for the organotin(IV)chlorides as follow: $Ph_2SnCl_2 > Me_2SnCl_2 > Bu_2SnCl_2 > Ph_3SnCl$ Adducts have been separately synthesized and fully characterized by ^{119}SnNMR, IR, Uv-Vis spectra and elemental microanalysis (C.H.N) methods. The trend of the rate constants for the adduct formation of the cobalt complexes with a given tin acceptor decreases as follow: [Co(amaen)] > [Co(appn)] > [Co(ampen)] > [Co(cappn)] > [Co(campen)]. The linear plots of k_{obs} *vs*. the molar concentration of the organotin(IV) chlorides, the high span of the second order rate costant k_2 values and the large negative values of $\Delta S^{\#}$ and low $\Delta H^{\#}$ suggest an associative (A) mechanism for the acceptor-donor adduct formation. Also [Co(aptn)]{[N,N'-1,3-propylenebis-(o-amino-α-phenylbenzylideneiminato)cobalt(II)] and [Co(captn)]{[N,N'-1,3-proylenebis-(5-chloro-o-amino-αphenylbenzylideneiminato)cobalt (II)]} were synthesized and characterized but their kinetics with R_2SnCl_2 were very fast that we were unable to follow them using the conventional methods.

Key words: Diorganotin(IV)dichlorides, Kinetic, Mechanism,
Tetraaza Schiff base, Cobalt(II) complex Triphenyltin(IV)chloride.

INTRODUCTION

Schiff bases form stable complexes with metals that perform an important role in biological systems[1]. Transition metal Schiff base complexes have many applications in the area of antitumoral, antiviral and antibacterial activity[2] and are also used as mimetic systems for enzyme models[3].

The tetraorganotin compounds show no evidence of Lewis acidity, the tin(IV) halides are strong Lewis acids which can produce 1:1 and 1:2

adducts in the presence of Lewis bases. The organotin halides R_nSnX_{4-n} are intermediate in Lewis acidity and found between R_4Sn and SnX_4. Generally the acidity is increased when the proportion of the halide is increased.

It is worth to note that till now no studies have been done on the kinetics and mechanism of the adduct formation between Co(II) tetraaza Schiff base complexes and the diorganotin(IV)dichlorides, although several studies have been done in our group on the thermodynamics of their adduct formation[4,5].

In this paper we have investigated the kinetics and mechanism of the interaction between the cobalt(II) tetraaza Schiff base complexes as donor and the organotin(IV)chlorides as acceptor. Cobalt(II) tetraaza Schiff base complexes such as [Co(ampen)], [Co(campen)], [Co(amaen)], [Co(cappn)] and [Co(appn)] were synthesized and characterized. The kinetics and mechanism of their adduct formation with diorganotin(IV)dichlorides, such as Me_2SnCl_2, Bu_2SnCl_2, Ph_2SnCl_2 and Ph_3SnCl as acceptors in DMF solvent were studied spectrophotometrically, and explained by an associative (A) mechanism.

EXPERIMENTAL

Reagents

1,2-ethylenediamine, 2-amino-5-chlorobenzophenone, 2-amino-benzophenone, 2-amino- acetophenone, 1,2-propylenediamine, methanol, chloroform, cobalt(II)acetatetetrahydrate, dimethyltin(IV)dichloride, dibutyltin(IV)dichloride, diphenyltin(IV)dichloride triphenyltin(IV)chloride and acetonitrile were commercially obtained from Merck , Fluka or Acros and used without further purification.

Instrument

Light-absorption measurements in the region (300-700 nm) were made with a Perkin-Elmer-Uv-Vis spectrophotometer-Lambda 2, equipped with a Lauda-ecoline-RE thermostat. FT-IR spectra were run on a Shimadzu FTIR-8300 spectrophotometer. ^{119}SnNMR spectra were recorded on a Bruker Avance DPX-400 spectrometer in $CDCl_3$ solvent. Elemental microanalyses (C.H.N.) were obtained using a Thermo Finnigan-CHNSO Analyzer.

Synthesis of Cobalt(II) Tetraaza Schiff Base Complexes

The four-coordinate complexes of N_4 type, [Co(amaen)], [Co(ampen)], [Co(campen)], [Co(appn)], [Co(cappn)], [Co(aptn)] and [Co(captn)] were prepared according to the literature [6] (Fig. 1). The IR and the Uv-Vis absorption spectra were in good agreement with the published data [6].

Synthesis of Adducts of Diorganotin(IV) dichlorides with Co(II) Tetraaza Schiff Base Complexes

0.1 mmol R_2SnCl_2 was dissolved in 5 ml acetonitrile and dropwisely added to 0.1 mmol of the Co(™™) complexes in 10 ml acetonitrile. The mixture was stirred for 2h at room temperature. During that time the red color solution was changed to green precipitate. Changing in color is due to the interaction of R_2SnCl_2 with Co(™™) complexes. The precipitate was filtered off and dried under vacuum (Fig. 2).

Kinetic Measurement

A solution from each Co(II) complex with certain concentration 6.4×10^{-5} M was prepared. In a typical measurement, 2.5 ml of this solution was transferred into the thermostated cell compartment of the Uv-Vis instrument, which was kept at constant temperature (runs from 10 – 40(± 0.1ºC)) by circulating water. Excess concentration in the range (1×10^{-4}- 4×10^{-2} M) of a given R_2SnCl_2 and (1.3×10^{-3}- 1.1×10^{-1} M) of Ph_3SnCl acceptor was added to this solution by Hamilton µL syringe.

The absorption measurements were carried out at various wavelengths where the different in absorptions were the maximum. The formed adduct shows absorption different from the donor, while the acceptors show no absorption at those wavelengths. The pseudo- first order rate constants k_{obs} (s^{-1}) were calculated by fitting the data to $\ln [(A_t - A_„)/(A_0 - A_„)] = k_{obs}t$ (where A_t = absorbance at time t; A_0 = absorbance at t = 0; $A_„$ = absorbance at t = ∞) by means of a linear least-squares computer program. The second-order rate constants k_2 ($M^{-1}s^{-1}$) were obtained from the slope of the linear plots of k_{obs} *vs.* [A] (acceptor concentration). The standard deviation values of the rate constants were obtained duplicate readings.

The activation parameters $\Delta H^{\#}$, $\Delta S^{\#}$ were obtained from the linear Eyring plots of $\ln(k_2/T)$ *vs*. 1/T at four different temperatures in the range (10-40ºC) using linear least squares computer program. Also the $\Delta G^{\#}$ values were computed by the same program using equation $\Delta G^{\#} = \Delta H^{\#} - T\,\Delta S^{\#}$ at T=313K.

RESULTS AND DISCUSSION

Spectral Characterization

Electronic Spectra

Absorption spectra of the Co(II) complexes and their adducts with diorganotin(IV)dichlorides were examined over the range 300-700 nm, in DMF solvent and the results are summarized in (Table 1). In Co(II) tetraaza Schiff base complex spectrum several intense absorption bands are observed in the Uv-Vis regions. By addition of R_2SnCl_2 to a solution of Co(II) tetraaza Schiff base complex in DMF the original peaks of Co(II) tetraaza Schiff base complex are changed. The electronic spectra of adducts formed at the end of the kinetic runs were the same as the electronic spectra of the respective separately synthesized adducts (Fig.3).

^{119}SnNMR Spectra

Holeček and coworkers studies show that the di- and tri-organotin ^{119}SnNMR spectra can be used as an indicator of the coordination number of the tin atom. In the ranges of +200 to -60, -90 to -190, -210 to -400, -440 to -540 ppm, the coordination number of the tin atom is four, five, six and seven, respectively[7-10]. The adducts formed in the present investigation exhibit the ^{119}Sn spectra in the range -110 to -182 ppm , suggesting that the tin atom is five-coordinated (Table 2).

IR Spectra

The stretching vibration of the azomethine group (C=N) is observed in the range (1610-1680 cm^{-1}). The stronger bands in the range (1440-1600 cm^{-1}) are due to the skeleton stretching vibration of

Table 1: The Uv-Vis bands λ_{max} (nm) of the cobalt(II) tetraaza complexes and their adducts with diorganotin(IV)dichlorides in DMF

Complex	λ (nm)
[Co(amaen)]	371, 428, 540
[Co(amaen)].(Ph_2SnCl_2).H_2O	366 (sh), 426
[Co(amaen)].(Me_2SnCl_2).H_2O	427 (sh)
[Co(amaen)].(Bu_2SnCl_2).H_2O	361 (sh), 423 (sh)
[Co(campen)]	387, 442, 552
[Co(campen)].(Ph_2SnCl_2).H_2O	384, 440, 554
[Co(campen)].(Me_2SnCl_2).H_2O	381, 439, 551
[Co(campen)].(Bu_2SnCl_2).H_2O	380, 439, 551
[Co(ampen)]	377, 436, 542
[Co(ampen)].(Ph_2SnCl_2).H_2O	369 (sh), 431
[Co(ampen)].(Me_2SnCl_2).H_2O	431 (sh)
[Co(ampen)].(Bu_2SnCl_2).H_2O	370 (sh), 431
[Co(appn)]	479, 438, 541
[Co(appn)].(Ph_2SnCl_2).H_2O	470 (sh), 432, 539 (sh)
[Co(appn)].(Me_2SnCl_2).H_2O	373 (sh), 432, 538 (sh)
[Co(appn)].(Bu_2SnCl_2).H_2O	369 (sh), 431, 536 (sh)
[Co(cappn)]	387, 442, 554
[Co(cappn)].(Ph_2SnCl_2).H_2O	384, 440, 553
[Co(cappn)].(Me_2SnCl_2).H_2O	370 (sh), 440, 552 (sh)
[Co(cappn)].(Bu_2SnCl_2).H_2O	384, 439, 551

C=C of the benzene ring. The band at about 400 cm^{-1} can be assigned to the (Co-N) vibration. This band is the characteristic band of the complexes and was not found in the free Schiff base ligand spectra. The results show that, by formation of adducts, the C=N vibrations are shifted toward higher frequencies about (13-25 cm^{-1}). The ring skeletal vibrations (C=C) are weakly affected by complexation. By formation of adducts, the (N-H) vibrations have been shifted toward higher frequencies. In the IR spectra of adducts, vibration bands in the range (3400-3450 cm^{-1}) as well as at (704-725 cm^{-1}) is assigned to (O-H) stretching of the coordinated H$_2$O present[11] in adduct formed (Table 3).

Table 2: ^{119}SnNMR characterization of some cobalt (II) adducts with diorganotindichlorides

^{119}Sn(δ,ppm)	Complex
-182.42	[Co(amaen)].(Ph$_2$SnCl$_2$).H$_2$O
-176.35	[Co(amaen)].(Me$_2$SnCl$_2$).H$_2$O
-168.33	[Co(amaen)].(Bu$_2$SnCl2).H2O
-110.12	[Co(campen)].(Ph$_2$SnCl$_2$).H$_2$O
-120.39	[Co(campen)].(Me$_2$SnCl$_2$).H$_2$O
-145.65	[Co(campen)].(Bu$_2$SnCl$_2$).H$_2$O
-165.54	[Co(ampen)].(Ph$_2$SnCl$_2$).H$_2$O
-143.25	[Co(ampen)].(Me$_2$SnCl$_2$).H$_2$O
-151.18	[Co(ampen)].(Bu$_2$SnCl$_2$).H$_2$O
-1889.0	[Co(appn)].(Ph$_2$SnCl$_2$).H$_2$O
-166.0	[Co(appn)].(Me$_2$SnCl$_2$).H$_2$O
-179.0	[Co(appn)].(Bu$_2$SnCl$_2$).H$_2$O
-142.0	[Co(cappn)].(Ph$_2$SnCl$_2$).H$_2$O
-120.0	[Co(cappn)].(Me$_2$SnCl$_2$).H$_2$O
-166.0	[Co(cappn)].(Bu$_2$SnCl$_2$).H$_2$O

Elemental Microanalysis

Elemental analysis of the synthesized products have good agreement with the proposed adducts of the kinetic runs with the stochiometric composition 1:1 for Co(II) tetraaza: R$_2$SnCl$_2$ with one coordinated H$_2$O molecule (Table 4).

Kinetic Studies

Tables (5-24) show the rate constants and the activation parameters for the kinetic interaction between diorganotin(IV)dichlorides and

Table 3: The IR bands characteristic of Co (II) tetraaza complexes and their adducts with diorganotin (IV) dichlorides

Compound	υ_{O-H}	υ_{N-H}	$\upsilon_{C=N}$	$\upsilon_{=C}$
[Co(amaen)]		3243	1551	1426-1503
[Co(amaen)].(Ph$_2$SnCl$_2$).H$_2$O	3398, 704	3220	1624	1450-1598
[Co(amaen)].(Me$_2$SnCl$_2$).H$_2$O	3402, 710	3205	1630	1450-1598
[Co(amaen)].(Bu$_2$SnCl$_2$).H$_2$O	3408, 725	3240	1635	1455-1595
[Co(campen)]		3262	1541	1387-1479
[Co(campen)].(Ph$_2$SnCl$_2$).H$_2$O	3434, 705	3170	1657	1459-1564
[Co(campen)].(Me$_2$SnCl$_2$).H$_2$O	3430, 708	3230	1674	1503-1561
[Co(campen)].(Bu$_2$SnCl$_2$).H$_2$O	3443, 783	3210	1650	1460-1569
[Co(ampen)]		3272	1599	1449-1556
[Co(ampen)].(Ph$_2$SnCl$_2$).H$_2$O	3422, 708	3212	1649	1455-1560
[Co(ampen)].(Me$_2$SnCl$_2$).H$_2$O	3446, 771	3213	1652	1456-1567
Co(ampen)].(Bu$_2$SnCl$_2$).H$_2$O	3421, 719	3205	1643	1453-1565
[Co(appn)]		3320	1599	1488-1551
[Co(appn)].(Ph$_2$SnCl$_2$).H$_2$O	3427, 781	3233	1561	1411-1508
[Co(appn)].(Me$_2$SnCl$_2$).H$_2$O	3456, 785	3233	1556	1416-1503
[Co(appn)].(Bu$_2$SnCl$_2$).H$_2$O	3427, 781	3243	1599	1517-1561
[Co(cappn)]		3320	1551	1407-1479
[Co(cappn)].(Ph$_2$SnCl$_2$).H$_2$O	3446, 708	3222	1556	1430-1498
[Co(cappn)].(Me$_2$SnCl$_2$).H$_2$O	3446, 708	3233	1561	1450-1503
[Co(cappn)].(Bu$_2$SnCl$_2$).H$_2$O	3427, 708	3213	1561	1455-1508

triphenyltin(IV)chloride with the cobalt(II) tetraaza Schiff base complexes in DMF as solvent at various temperatures. The kinetics were followed under pseudo-first-order conditions for the acceptor concentration; the donor concentration was kept constant at 6.4×10^{-5} M, and the excess concentration of each acceptor was varied in the range 1×10^{-4}-4×10^{-2} M. The results in Tables (5-24) show that there is a linear rate dependence on the concentration of the acceptor [A].

Since most of the kinetic studies[12] that have been published till now were carried out in interfering (i.e. coordinating) solvents, it is necessary to investigate the nature of this interference before the mechanistic assignment is secure[13]. Plots of k_{obs} *vs.* R_2SnCl_2 and plots of k_{obs} vs. Ph_3SnCl exhibit an almost zero intercept. The present studies indicate that solvolysis of Co(II) tetraaza in DMF is negligible. Typical plots of k_{obs} vs. Ph_2SnCl_2 molar concentrations [A] for [Co(ampen)] at different temperatures are shown in Fig.4.

The isosbestic points observed for the reaction of R_2SnCl_2 with [Co(campen)] were at (588, 354 nm), with [Co(ampen)] were at (576, 343 nm) and with [Co(amaen)] were at (574, 343 nm). As an example, the variation of the electronic spectra for [Co(amaen)], reacted with excess Ph_2SnCl_2 at 30ºC in DMF is shown in Fig. 5. The isosbestic points show that there is only one reaction in progress. The same procedure was followed for other systems and similar results were observed.

Adduct entities were obtained from the reaction of the acceptors with the donors, according to Eq. (1):

$$[Co(L)]\cdot H_2O + R_2SnCl_2 \text{ or } Ph_3SnCl \rightarrow [Co\ (L)]\cdot(R_2SnCl_2)\cdot H_2O \text{ or } [Co\ (L)].(Ph_3SnCl).H_2O \quad ...(1)$$

Table 4: Elemental analytical data of tetraaza Schiff base complexes and their diorganoltin(IV)dichloride adducts.

Compound	Found (Calc.) (%)		
	N	H	C
[Co(amaen)]	15.55 (15.95)	5.34 (5.74)	61.11 (61.54)
[Co(amaen)].(Ph_2SnCl_2).H_2O	8.22 (8.76)	4.62 (4.52)	50.16 (50.53)
[Co(amaen)].(Me_2SnCl_2).H_2O	9.17 (9.51)	4.39 (4.79)	40.39 (40.78)
[Co(amaen)].(Bu_2SnCl_2).H_2O	8.62 (8.30)	6.11 (6.27)	45.92 (46.25)
[Co(campen)]	10.10(10.29)	3.98 (4.07)	61.49 (61.78)
[Co(campen)].(Ph_2SnCl_2).H_2O	6.50 (6.18)	4.01 (3.78)	52.67 (53.02)
[Co(campen)].(Me_2SnCl_2).H_2O	7.40 (7.16)	3.98 (3.87)	46.39 (46.08)
[Co(campen)].(Bu_2SnCl_2).H_2O	6.50 (6.45)	5.01 (5.11)	49.41 (49.80)
[Co(campen)]·(Bu_2SnCl_2)·H_2O (2c)			
[Co(ampen)]	11.44 (11.78)	5.34 (5.09)	70.51 (70.73)
[Co(ampen)].(Ph_2SnCl_2).H_2O	7.01 (9.37)	4.29 (4.10)	57.14 (57.52)
[Co(ampen)].(Me_2SnCl_2).H_2O	7.49 (7.86)	4.21 (4.52)	50.85 (50.53)
[Co(ampen)].(Bu_2SnCl_2).H_2O	7.39 (7.01)	5.49 (5.80)	53.89 (54.10)
[Co(appn)]	11.24 (11.45)	5.43 (5.35)	71.30 (71.16
[Co(appn)].(Ph_2SnCl_2).H_2O	6. 40 6.58)	4.35 (4.50)	57.55 (57.85)
[Co(appn)].(Me_2SnCl_2).H_2O	7. 88 (8.13)	6.32 (6.43)	46.87 (47.05)
[Co(appn)].(Bu_2SnCl_2).H_2O	7.31 (7.70)	4.52 (4.71)	50.95(51.20)
[Co(cappn)]	10.18 (10.03)	4.29 (4.33)	61.98 (62.38)
[Co(cappn)].(Ph_2SnCl_2).H_2O			
[Co(cappn)].(Me_2SnCl_2).H_2O (**2b**)	6.35 (6.09)	3.71 (3.94)	53.22 (53.52)
[Co(cappn)].(Bu_2SnCl_2).H_2O (**2c**)	7.56 (7.39)	5.86 (5.58)	42.46 (42.78)
[Co(cappn)].(Bu_2SnCl_2).H_2O	6.74 (7.04)	4.23 (4.05)	46.42 (46.77)

Table 5: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(campen) with Ph_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	2.5	5.0	7.6	10.0	12.6	15.1	17.6	20.1	$10^2k_2/M^{-1}s^{-1}$
10°C	1.6 (0.0)	4.2 (0.0)	5.8 (0.1)	7.8 (0.2)	10.4 (0.4)	12.4 (0.3)	13.5 (0.8)	16.1 (0.7)	80.8 (2.3)
20°C	2.3 (0.0)	5.5 (0.0)	7.6 (0.1)	10.2 (0.2)	12.4 (0.8)	14.0 (0.3)	16.8 (0.8)	18.6 (0.4)	90.0 (3.0)
30°C	3.5 (0. 0)	6.4 (0.0)	9.4 (0.6)	12.0 (0.7)	15.2 (1.6)	17.7 (0.8)	20.9 (1.0)	24.5 (1.3)	117.0 (2.0)
40°C	4.2 (0.2)	7.5 (0.1)	11.4 (0.4)	15.2 (0.1)	17.4 (0.0)	21.3 (1.0)	25.4 (1.1)	28.7 (1.1)	138.0 (3.0)

Table 6: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(campen) with Me_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	0.7	1.4	2.2	2.9	3.6	4.3	5.0	5.8	$10^2k_2/M^{-1}s^{-1}$
10°C	0.4 (0.0)	0.6 (0.0)	0.9 (0.1)	0.9 (0.0)	1.0 (0.1)	1.3 (0.3)	1.3 (0.2)	1.7 (0.3)	22.0 (1.4)
20°C	0.7 (0.0)	1.0 (0.1)	1.6 (0.2)	1.9 (0.8)	2.0 0.3)	2.3 (0.0)	2.5 (0.0)	2.7 (0.2)	39.0 (2.9)
30°C	1.1 (0.2)	1.6 (0.4)	2.3 (0.3)	2.8 (0.0)	3.3 (0.2)	3.7 (0.8)	4.2 (1.1)	4.6 (1.2)	63.6 (1.7)
40°C	1.6 (0.3)	2.0 (0.3)	2.8 (0.5)	3.5 (0.7)	4.3 (0.6)	4.8 (1.0)	5.2 (1.1)	5.7 (1.1)	71.0 (2.6)

Table 7: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co (campen) with Bu_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	0.7	1.4	2.2	2.9	3.6	4.3	5.0	5.8	$10^2k_2/M^{-1}s^{-1}$
10°C	0.1 (0.0)	0.6 (0.0)	1.3 (0.1)	1.6 (0.6)	2.5 (0.1)	3.3 (0.3)	4.1 (0.2)	4.9 (0.3)	27.0 (1.2)
20°C	0.5 (0.0)	0.9 (0.1)	1.9 (0.2)	2.5 (0.3)	3.2 (0.3)	4.1 (0.3)	4.9 (0.1)	5.5 (0.6)	30.0 (0.8)
30°C	0.8 (0.1)	1.7 (0.2)	2.3 (0.3)	3.4 (0.1)	4.2 (0.2)	5.0 (0.8)	5.7 (0.4)	6.5 (1.2)	33.0 (0.7)
40°C	1.3 (0.2)	2.2 (0.4)	3.8 (0.5)	4.4 (0.0)	5.5 (0.7)	6.4 (1.0)	7.2 (1.1)	8.1 (1.1)	39.0 (1.2)

Table 8: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(ampen) with Ph_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	2.5	5.0	7.6	10.1	12.6	15.1	17.6	20.1	$10^2k_2/M^{-1}s^{-1}$
10°C	1.4 (0.0)	3.1 (0.2)	6.1 (0.4)	8.0 (0. 5)	9.9 (0.8)	12.0 (0.7)	14.9 (0.9)	16.8 (0.1)	87.0 (4.0)
20°C	3.0 (0.1)	5.1 (0.2)	8.2 (0.5)	10.7 (0.6)	13.5 (0.9)	16.7 (0.9)	19.7 (1.3)	22.1 (0.9)	110.3 (1.6)
30°C	3.2 (0.1)	7.7 (0.4)	11.4 (1.0)	13.6 (0.5)	17.2 (1.2)	20.3 (1.3)	26.8 (1.2)	29.9 (1.2)	147.2 (6.1)
40°C	4.9 (0.0)	8.6 (0.3)	13.2 (1.2)	17.9 (2.4)	22.3 (1.1)	28.2 (1.1)	33.3 (1.1)	39.9 (1.1)	196.0 (6.4)

Table 9: Pseudo -First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co (ampen) with Me_2SnCl_2 in DMF at Different TTemperatTemperature. [Complex]= 6.4×10^{-5}M

10^3[A]/M	0.7	1.4	2.2	2.9	3.6	4.3	5.0	5.8	$10^2k_2/M^{-1}s^{-1}$
10°C	1.5 (0.0)	1.9 (0.1)	2.4 (0.0)	3.0 (0. 0)	3.6 (0.1)	4.4 (0.1)	4.9 (0.2)	5.0 (0.2)	75.0 (3.6)
20°C	1.9 (0.0)	2.5 (0.0)	3.1 (0.1)	3.8 (0.1)	4.5 (0.1)	5.5 (0.1)	5.9 (0.0)	6.2 (0.2)	92.0(3.7)
30°C	2.5 (0.0)	3.3 (0.0)	3.8 (0.0)	4.6 (0.2)	5.4 (0.0)	6.5 (0.0)	8.2 (0.5)	9.3 (.02)	133.0 (0.1)
40°C	3.1 (0.0)	3.9 (0.0)	4.7 (0.0)	6.0 (0.1)	6.9 (0.4)	7.8 (0.7)	9.0 (0.1)	10.0 (0.1)	146.0 (1.8)

Table 10: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(ampen) with Bu_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	5.0	10.0	15.1	20.1	25.2	30.2	35.2	40.3	$10^2k_2/M^{-1}s^{-1}$
10°C	1.1 (0.0)	2.8 (0.0)	4.0 (1.1)	5.1 (0 1)	6.6 (0.5)	7.9 (0.1)	9.5 (0.2)	11.5 (0.4)	28.0 (0. 8)
20°C	2.2 (0.0)	3.9 (0.2)	5.2 (0.2)	6.8 (0.1)	8.9 (0.7)	10.0 (0.4)	12.1 (0.6)	14.6 (0.8)	34.0 (1.1)
30°C	3.4 (0.0)	5.8 (0.1)	6.6 (0.3)	9.4 (0.5)	12.8 (1.3)	16.0 (0.3)	17.8 (2.7)	19.1 (0.0)	47.0 (2.7)
40°C	4.4 (0.1)	8.3 (0.2)	10.9 (0.6)	13.7 (0.5)	16.6 (0.7)	19.9 (0.4)	22.2 (0.2)	26.2 (1.0)	59.0 (1.3)

Table 11: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a(s^{-1})$ for the Reaction of Co(amaen) with Ph_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	0.1	0.2	0.3	0.4	0.5	0.5	0.6	$10^2k_2/M^{-1}s^{-1}$
10ºC	11.1 (0. 5)	14.0 (0. 8)	17.4 (0. 6)	19.2 (1.1)	21.9 (0.1)	25.4 (0.2)	27.9 (0.7)	3632.0 (73.0)
20ºC	12.4 (0.9)	14.9 (0.6)	17.5 (0.4)	21.5 (0.4)	23.6 (0.9)	28.3 (0.9)	30.1 (0.9)	3906.0 (119.0)
30ºC	14.0 (0.7)	16.1 (0.6)	19.1 (0.7)	24.5 (0.7)	27.0 (0.9)	30.8 (0.9)	34.3 (0.2)	4549.0 (131.0)
40ºC	15.4 (0.9)	18.2 (0.5)	22.7 (0.9)	27.4 (0.9)	32.5 (0.8)	37.2 (0.7)	42.7 (0.9)	5761.0 (219.0)

Table 12: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a(s^{-1})$ for the Reaction of Co(amaen) with Me_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	5.0	10.0	15.1	20.1	25.2	30.2	35.2	40.3	$10^2k_2/M^{-1}s^{-1}$
10ºC	1.9 (0.0)	5.3 (0.0)	8.6 (0.1)	12.6 (0.5)	14.7 (0.5)	18.5 (0.5)	20.4 (0.9)	23.0 (0.9)	1398.0 (46.0)
20ºC	4.3 (0.3)	8.6 (0.4)	11.3 (0.7)	15.2 (0.9)	18.5 (0.7)	22.1 (0.8)	24.8 (0.9)	27.5 (0.9)	1528.0 (34.0)
30ºC	7.7 (0.0)	11.3 (0.4)	14.5 (0.9)	18.7 (0.2)	22.0 (0.2)	25.0 (0.3)	28.9 (0.9)	32.5 (0.9)	1622.0 (19.0)
40ºC	11.4 (0.2)	15.4 (0.6)	18.5 (0.8)	22.2 (0.8)	26.8 (0.9)	29.5 (0.8)	33.5 (0.9)	38.5 (0.9)	1740.0 (39.0)

Table 13: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(amaen) with Bu_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	0.2	0.4	0.6	0.8	1.0	1.1	1.3	1.5	$10^2k_2/M^{-1}s^{-1}$
10ºC	9.0 (0.3)	11.3 (0.5)	14.1(0.5)	16.0 (0.9)	17.8 (1.4)	19.7 (0.3)	22.7 (0.9)	24.5 (1.1)	1161(24.0)
20ºC	10.2 (0.5)	12.5 (0.6)	15.5 (0.8)	17.9 (0.4)	19.7 (1.0)	22.3 (2.0)	24.8 (0.3)	27.3 (0.7)	1260 (26.0)
30ºC	12.5 (0.3)	15.2 (0.7)	17.6 (1.1)	20.0 (1.4)	22.3 (2.0)	25.0 (1.0)	27.5 (0.9)	29.5 (0.5)	1287 (12.0)
40ºC	14.4 (0.8)	17.2 (1.7)	21.3 (0.9)	23.9 (0.9)	26.4 (0.7)	28.7 (1.0)	30.9 (0.9)	33.1 (0.9)	1373 (54.0)

Table 14: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(cappn) with Ph_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	3.8	5.1	6.4	7.7	9.0	10.2	11.5	12.8	$10^2k_2/M^{-1}s^{-1}$
10°C	2.0 (0.3)	4.0 (0.4)	7.0 (0.5)	9.0 (0.5)	11.0 (1.5)	13.4 (3.0)	15.6 (1.7)	18.0 (3.2)	177.0 (2.7)
20°C	3.6 (3.7)	6.3 (0.5)	8.6 (0.4)	11.0 (0.2)	14.0 (0.6)	19.0 (0.3)	23.0 (0.8)	23.0 (0.3)	211.0 (5.7
30°C	4.5 (0.4)	8.1 (0.4)	11.2(1.1)	14.2 (2.1)	17.8(2.9)	20.0 (2.8)	23.5 (3.2)	27.2 (1.3)	246.0 (3.0)
40°C	5.5 (0.3)	11.0 (0.3)	15.5 (0.4)	18.0 (0.7)	22.0 (0.7)	25.0 (0.6)	29.0 (3.3)	33.8 (2.2)	303.0 (7.0)

Table 15: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(cappn) with Me_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	3.8	5.1	6.4	7.7	9.0	10.2	11.5	12.8	$10^2k_2/M^{-1}s^{-1}$
10°C	1.0 (0.1)	1.8 (0.0)	3.2 (0.0)	3.9 (0.1)	4.7 (0.2)	5.9 (0.5)	6.8 (0.7)	7.8 (0.3)	75.0 (1.8)
20°C	1.2 (0.0)	3.0 (0.1)	4.2 (0.2)	5.4 (0.5)	6.9 0.4)	8.8 (0.9)	9.8 (0.9)	12.0 (1.52)	115.0 (3.7)
30°C	2.0 (0.0)	4.5 (0.2)	6.7 (0.5)	8.2 (0.7)	10.4 (1.3)	12.2 (1.1)	14.3 (2.2)	17.4 (4.3)	162.0 (4.7)
40°C	3.6 (0.4)	6.0 (0.7)	8.2(0.8)	11.0 (0.9)	14.1 (1.8)	16.5 (2.7)	18.9 (2.8)	21.58 (5.9)	202.0 (3.0)

Table 16: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(cappn) with Bu_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	3.8	5.1	6.4	7.7	9.0	10.2	11.5	12.8	$10^2k_2/M^{-1}s^{-1}$
10°C	0.1 (0.0)	0.3 (0.0)	0.7 (0.0)	1.1 (0.0)	1.4 (0.0)	1.8 (0.0)	2.1 (0.0)	2.5 (0.0)	27.0 (0.5)
20°C	0.15 (0.0)	0.5 (0.0)	0.09 (0.0)	1.3 (0.0)	1.6 (0.0)	2.0 (0.0)	2.4(0.1)	3.0 (0.1)	30.2 (0.6)
30°C	0.2 (0.0)	0.7 (0.0)	1.1(0.0)	1.6 (0.1)	2.0 (0.1)	2.4 (0.1)	2.9 (0.2)	3.4 (0.3)	35.1 (0.3)
40°C	0.3 (0.1)	0.8 (0.2)	1.3 (0.2)	1.9 (0.50)	2.5 (0.3)	3.0 (0.5)	3.6 (0.71)	4.1 (0.5)	42.3 (0.4)

Table 17: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(appn) with Ph_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	0.6	1.3	1.9	2.6	3.2	3.8	4.5	5.1	$10^2k_2/M^{-1}s^{-1}$
10°C	5.5 (0.1)	7.2 (0.2)	9.6 (0.2)	12.3 (1.4)	15.1 (1.5)	17.5 (2.7)	20.0 (1.5)	23.0 (1.6)	397.0 (9.0)
20°C	7.3 (0.1)	9.6 (0.2)	13.0 (0.9)	17.6 (1.3)	20.0 (1.3)	23.4 (1.2)	26.7(1.4)	30.0 (2.4)	519.0 (10.0)
30°C	9.1 (1.3)	12.0 (0.9)	16.0 (1.0)	19.5 (1.3)	25.0 (3.0)	29.7 (1.6)	33.0 (2.5)	36.4 (4.5)	637.0 (10.0)
40°C	11.0 (0.6)	16.2 (1.8)	19.4 (1.9)	25.1 (2.3)	29.8 (2.9)	35.7 (2.8)	42.6 (3.5)	47.3 (2.1)	819.0 (15.0)

Table 18: Pseudo -First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(appn) with Me_2SnCl_2 in DMF at Different TTemperatTemperature. [Complex]= 6.4×10^{-5}M

10^3[A]/M	0.6	1.3	1.9	2.6	3.2	3.8	4.5	5.1	$10^2k_2/M^{-1}s^{-1}$
10°C	1.0 (0.0)	2.1(0.1)	3.3 (0.0)	4.5 (0. 1)	5.7(0.1)	6.4 (0.0)	7.4(0.1)	8.5 (0.1)	167.0 (4.0)
20°C	2.5 (0.0)	3.9 (1.6)	5.2 (0.5)	7.4 (2.4)	9.1 (1.2)	10.0 (1.4)	11.2 (1.2)	13.0 (0.7)	235.0 (8.0)
30°C	3.7 (0.1)	5.9 (1.0)	7.3 (1.1)	9.5 (2.5)	12.0 (0.7)	14.0 (.0.9	15.2 (0.2)	17.6 (0.2)	310.0 (8.0)
40°C	5.0 (0.0)	8.1(0.0)	9.8 (0.1)	12.4 (0.2)	15.6 (0.2)	17.9 (0.2)	20.0 (0.3)	22.0 (0.4)	384.0 (10.0)

Table 19: Pseudo-First-Order Rate Constants $10^3k_{obs}{}^a$ (s^{-1}) for the Reaction of Co(appn) with Bu_2SnCl_2 in DMF at Different Temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	0.6	1.3	1.9	2.6	3.2	3.8	4.5	5.1	$10^2k_2/M^{-1}s^{-1}$
10°C	0.5 (0.0)	0.9 (0.0)	1.2 (0.0)	1.4 (0 2)	1.7 (0.0)	2.0 (0.0)	2.3 (0.0)	2.5 (0.1)	42.80 (0.9)
20°C	0. 6 (0.0)	1.0(0.2)	1.3 (0.2)	1.7 (0.0)	1.9 (0.0)	2.2 (0.1)	2.5 (0.0)	2.9 (0.2)	49.7 (1.0)
30°C	0.7 (0.2)	1.2(1.2)	1.5 (1.9)	1.9 (2.1)	2.2(0.8)	2.6 (1.4)	3.0 (2.0)	3.5 (0.0)	59.0 (1.4)
40°C	0.9 (0.1)	1.3 (0.1)	1.8 (0.8)	2.5 (1.4)	2.9 (2.2)	3.5 (2.2)	3.9 (0.9)	4.5 (1.1)	81.4 (1.8)

Table 20: Pseudo-first-order rate constants $10^3k_{obs}{}^a$ (s^{-1}) for the reaction of Co(amaen) with Ph_3SnCl in DMF at different temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	1.3	2.6	3.8	5.1	6.4	7.7	9.0	10.2	10^2k_2/$M^{-1}s^{-1}$
10ºC	3.2 (0.0)	7.1 (0.0)	10.8 (0.1)	13.3 (0.2)	17.7 (0.4)	22.0 (0.3)	26.3 (0.8)	28.4 (0.7)	289.0 (7.0)
20ºC	3.7 (0.0)	8.3 (0.0)	12.6 (0.1)	16.2 (0.2)	21.4 (0.8)	25.8 (0.3)	30.0 (0.8)	34.5 (0.4)	343.0 (3.6)
30ºC	4.6 (0. 0)	9.7 (0.0)	16.5 (0.6)	21.0 (0.7)	26.4 (1.6)	32.1 (0.8)	36.7 (1.0)	42.8 (1.3)	423.0 (7.0)
40ºC	5.7 (0.2)	13.2 (0.1)	19.2 (0.4)	26.4 (0.1)	34.2 (0.0)	42.0 (1.0)	47.8 (1.1)	55.4 (1.1)	556.0 (6.0)

Table 21: Pseudo-first-order rate constants $10^3k_{obs}{}^a$ (s^{-1}) for the reaction of Co(appn) with Ph_3SnCl in DMF at different temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	7.7	11.5	15.3	19.2	23.0	26.8	30.7	34.5	10^2k_2/$M^{-1}s^{-1}$
10ºC	2.5(0.0)	4.3(0.0)	5.5(0.1)	6.5(0.0)	7.2(0.1)	7.9(0.3)	9.0(0.2)	10.0(0.3)	30.0(1.0)
20ºC	2.7(0.0)	4.9(0.1)	6.8(0.2)	8.7(0.8)	9.8(0.3)	12.0(0.0)	13.7(0.0)	15.5(0.2)	46.7(0.9)
30ºC	3.6(0.2)	5.7(0.4)	8.1(0.3)	10.7(0.0)	13.1(0.2)	15.3(0.8)	17.4(1.1)	18.5(1.2)	58.1(1.8)
40ºC	3.8(0.3)	6.9(0.3)	9.2(0.5)	12.5(0.7)	16.1(0.6)	18.7(1.0)	20.5(1.1)	23.0(1.1)	72.9(2.3)

Table 22: Pseudo-first-order rate constants $10^3k_{obs}{}^a$ (s^{-1}) for the reaction of Co(ampen) with Ph_3SnCl in DMF at different temperatures.[Complex]= 6.4×10^{-5}M

10^3[A]/M	2.6	5.1	7.7	10.2	12.8	15.3	17.9	20.0	10^2k_2/$M^{-1}s^{-1}$
10ºC	0.1(0.0)	1.6(0.0)	2.5(0.1)	3.2(0.6)	3.7(0.1)	4.5(0.3)	4.9(0.2)	5.2(0.3)	24.8(0.9)
20ºC	1.2(0.0)	2.0(0.1)	2.9(0.2)	3.6(0.3)	4.3(0.3)	5.4(0.3)	5.9(0.1)	6.2(0.6)	29.8(1.0)
30ºC	1.6(0.1)	2.7(0.2)	3.4(0.3)	4.5(0.1)	5.3(0.2)	6.3(0.8)	7.0(0.4)	7.5(1.2)	34.4(1.0)
40ºC	1.9(0.2)	3.1(0.4)	4.3(0.5)	5.5(0.0)	6.9(0.7)	7.7(1.0)	8.6(1.1)	9.7(1.1)	44.4(1.1)

Table 23: Pseudo-first-order rate constants $10^3k_{obs}{}^{a}$ (s^{-1}) for the reaction of Co(cappn) with Ph_3SnCl in DMF at different temperatures. [Complex]= 6.4×10^{-5}M

10^3[A]/M	20.5	38.4	51.2	64.0	76.8	89.6	102.0	115.0	$10^2k_2/M^{-1}s^{-1}$
10°C	6.0(0.0)	6.9(0.2)	9.2(0.4)	11.0(0. 5)	12.5(0.8)	14.2(0.7)	16.1(0.9)	17.9(0.1)	13.5(0.3)
20°C	6.2(0.1)	8.0(0.2)	11.0(0.5)	13.8(0.6)	15.8(0.9)	17.6(0.9)	19.7(1.3)	22.5(0.9)	18.1(0.5)
30°C	6.6(0.1)	9.9(0.4)	13.7(1.0)	16.4(0.5)	19.7(1.2)	23.5(1.3)	27.9(1.2)	31.0(1.2)	27.3(0.6)
40°C	7.0(0.0)	11.0(0.3)	16.2(1.2)	20.7(2.4)	24.5(1.1)	30.0(1.1)	34.2(1.1)	37.8(1.1)	35.0(0.5)

Table 24: Pseudo-first-order rate constants $10^3k_{obs}{}^{a}$ (s^{-1}) for the reaction of Co(campen) with Ph_3SnCl in DMF at different temperatures.[Complex]= 6.4×10^{-5}M

10^3[A]/M	20.5	38.4	51.2	64.0	76.8	89.6	102.0	115.0	$10^2k_2/M^{-1}s^{-1}$
10°C	2.6 (0.0)	3.9 (0.1)	4.5 (0.0)	5.6 (0. 0)	6.8 (0.1)	7.7 (0.1)	8.3 (0.2)	9.1 (0.2)	7.3 (0.2)
20°C	2.9 (0.0)	4.3 (0.0)	5.8 (0.1)	7.1 (0.1)	8.7 (0.1)	10.0 (0.1)	11.2 (0.0)	12.6 (0.2)	10.8 (0.0)
30°C	3.1 (0.0)	5.6 (0.0)	7.2 (0.0)	8.7 (0.2)	10.4 (0.0)	12.8 (0.0)	13.9 (0.5)	15.7 (0.0)	13.8 (0.3)
40°C	3.4 (0.0)	6.2 (0.0)	8.66 (0.0)	10.3(0.1)	13.4 (0.4)	15.1 (0.7)	17.2 (0.1)	19.3 (0.1)	17.5 (0.3)

a) The numbers in parentheses are the standard deviations of kobs.

Table 25: Activation Parameters[a] $\Delta G^{\#}$, $\Delta H^{\#}$ and $\Delta S^{\#}$ for the Reaction of Cobalt(™™) Complexes with Diorganotindichlorides in DMF

Adduct	$\Delta G^{\#}$” kJ.mol^{-1}	$\Delta H^{\#}$” kJ.mol^{-1}	$\Delta S^{\#}$”JK^{-1}.mol^{-1}
Ph_2SnCl_2			
Co(amaen) (1a)	66.4 (4.0)	10.0 (2.8)	-180.1 (9.4)
Co(ampen) (2a)	75.2 (1.3)	17.5 (0.9)	-184.3 (3.1)
Co(campen) (3a)	76.0 (0.5)	11.2 (0.4)	-207.8 (1.3)
Me_2SnCl_2			
Co(amaen) (1b)	69.5 (0.4)	2.8 (0.3)	-212.9 (0.9)
Co(ampen) (2b)	75.8 (3.6)	15.0 (2.6)	-194.2 (8.3)
Co(campen) (3b)	77.5 (7.3)	27.3 (5.0)	-160.5 (16.9)
Bu_2SnCl_2			
Co(amaen) (1c)	70.1 (0.8)	1.4 (0.6)	-219.4 (1.9)
Co(ampen) (2c)	78.3 (2.0)	16.4 (1.4)	-197.8 (4.7)
Co(campen) (3c)	79.4 (1.4)	6.3 (0.9)	-233.5 (6.8)
Ph_2SnCl_2			
Co(appn) (1a)	71.4 (0.8)	15.0 (0.6)	-180.2 (1.9)
Co(cappn) (2a)	74.1 (1.0)	10.5 (0.7)	-203.0 (2.5)
Me_2SnCl_2			
Co(appn) (1b)	73.3 (1.6)	18.3 (1.16)	-175.7 (3.7)
Co(cappn) (2b)	75.0 (2.8)	22.0 (1.9)	-169.0 (6.5)
Bu_2SnCl_2			
Co(appn) (1c)	77.6 (3.5)	12.9 (2.4)	-206.6 (8.0)
Co(cappn) (2c)	79.2(1.7)	8.6 (1.2)	-225.5 (3.9)

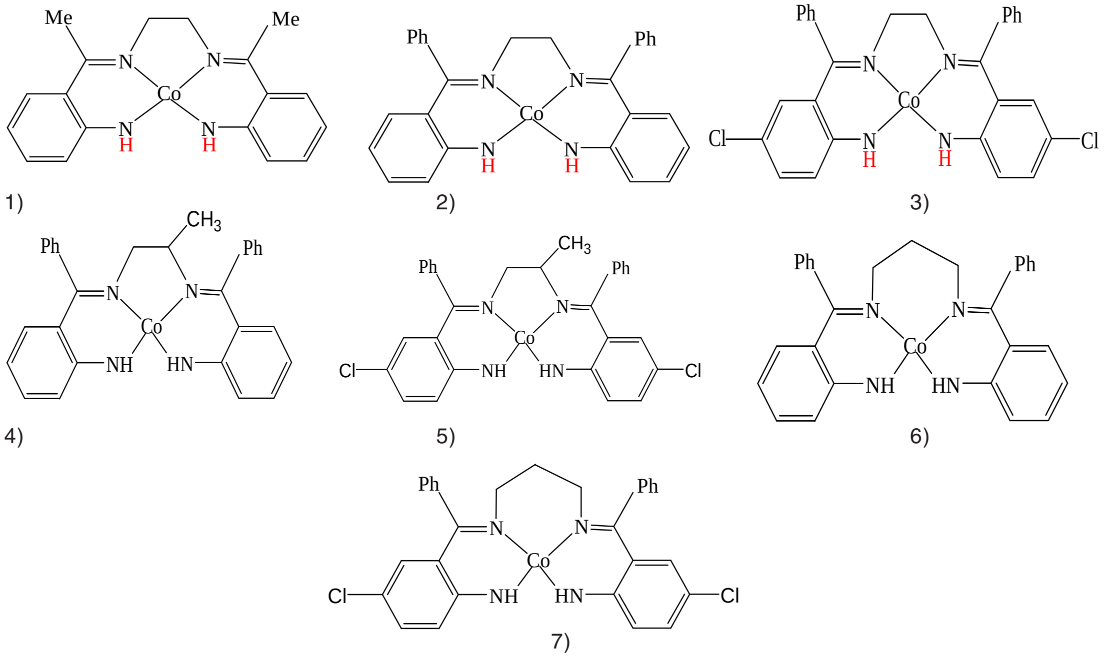

Fig. 1: The structure of [Co(amaen)] (1), [Co(ampen)] (2), [Co(campen)] (3), [Co(appn)] (4), [Co(cappn)] (5), [Co(aptn)] (6) and [Co(captn)] (7)

where L = campen, ampen, amaen, appn, cappn and R = Me, Bu, Ph.

The rate law of Eq. (2) is compatible with the adduct formation according to Eq. (1):

$$k_{obs} = k_2\,[A] \qquad ...(2)$$

The activation parameters, $\Delta H^{\#}$ and $\Delta S^{\#}$ (Table 25) were calculated as a function of temperature by Eyring Eq. (3):

$$\ln (k_2/T) = -\Delta H^{\#}/RT + \Delta S^{\#}/R + 23.8 \qquad ...(3)$$

A typical linear Eyring plots of $\ln(k_2/T)$ *vs.* 1/T at four different temperatures in the range (10-40ºC) for Co(ampen) donor with different acceptors is shown in Fig. 6. The Eyring plots for the reaction of different donors with the acceptor Ph_3SnCl (Lewis acid) in DMF is shown in Fig. 7.The low ”$H^{\#}$ values and the large negative $DS^{\#}$ values is compatible with (A) mechanism. Also the linear plots of k_{obs} *vs.* R_2SnCl_2 and or Ph_3SnCl the high span of k_2 values differing with the nature of the acceptors suggest an associative (A) mechanism.

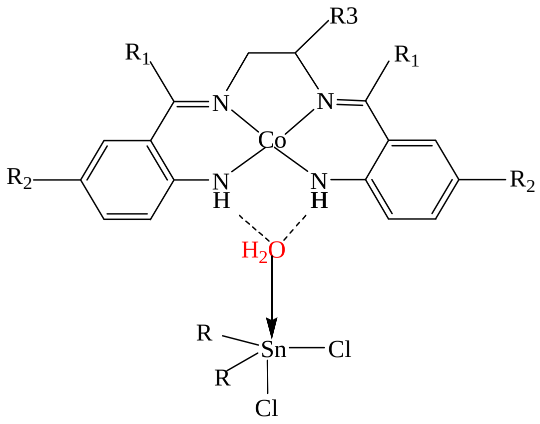

Fig. 2: The proposed structure of the adduct fromed in the kinetic reaction of R_2SnCl_2 with Co (II) tetraaza Schiff base complexes (R=Me, Bu, Ph, R_1=Me, Ph, R_2=H, Cl,R_3=Me)

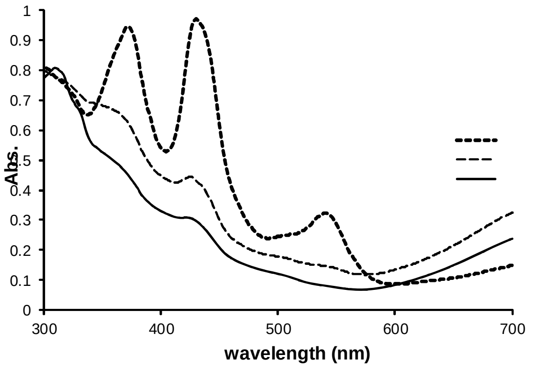

Fig. 3: The electronic spectra of the four-coordinate Co(amaen) (1), the separately synthesized adduct of Bu_2SnCl_2 with Co (amaen) (2) and the end of the kinetics of Co(amaen) with Bu_2SnCl_2 (3)

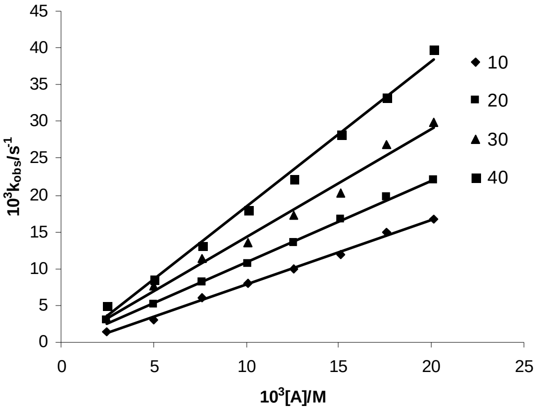

Fig.4: The plots of k_{obs} vs. Ph_2SnCl_2 molar concentrations [A] for [Co(ampen)] at different temperatures

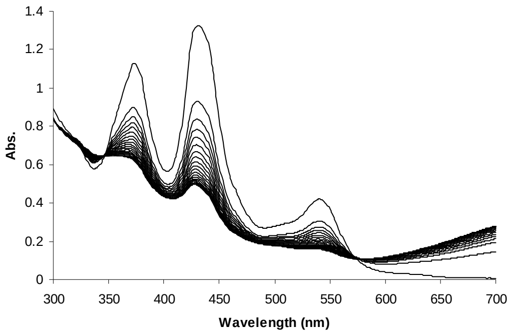

Fig. 5: The absorption spectra of the kinetics of [Co(amaen)], with twelve fold excess Ph_2SnCl_2 at 30ºC in DMF with the isosbestic points

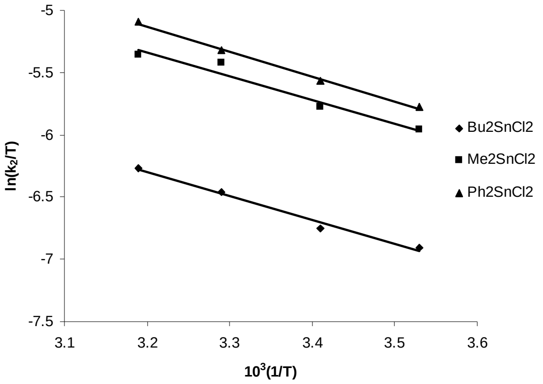

Fig. 6: The *Ey*ring plots for the reaction of different acceptors (Lewis acid) with Co (ampen) in DMF

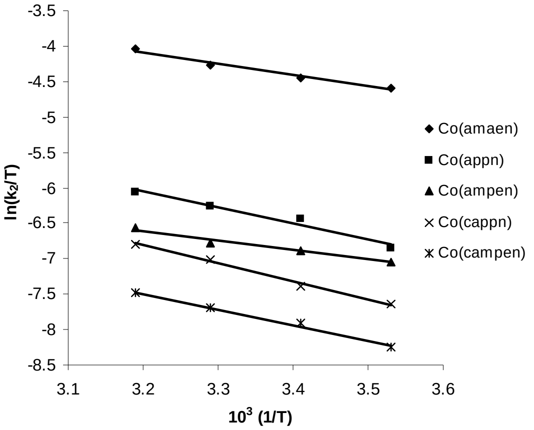

Fig. 7: The Eyring plots for the reaction of different donors with the acceptor Ph_3SnCl (Lewis acid) in DMF

The Acceptor Properties of the Diorganotin(IV) dichlorides and Triphenyltin(IV)chloride

Comparing the k_2 values, the following trend of acidity for the acceptors used was assessed: Ph_2SnCl_2 > Me_2SnCl_2 > Bu_2SnCl_2 > Ph_3SnCl.

It is clear that the electron withdrawing groups (Ph-) on the tin center makes Ph_2SnCl_2 a stronger Lewis acid than the others. This trend also indicates that replacing the methyl- by a more bulky butyl- group on the organotin(IV) compound causes a weakening of the interaction. The butyl- group can affect the interaction in two ways: 1) A more bulky butyl- group makes adduct formation unfavorable because of its greater steric hindrance than a methyl- group[14]. 2) Butyl- group, though, have better electron releasing properties to reduce the acid strength of the di-organotin(IV) Lewis acid but its steric effect would predominate and compensates the higher electronic effect. Although the electronic effect signifies that the k_2 values must be higher with the triphenyltin(IV)chloride , but its steric effect is predominating (see Table 7)[15]. These are compitable with the electronegativity of Ph=2.717, and Cl=3.0 in Pauling and 3.475 in Sanderson's scales[16].

Comparing the Donor Property of the Cobalt(II) Tetraaza Schiff Base Complexes

The k_2 values for the ligands entry show high span, suggesting the dependence of rate on the nature of the ligand. The low $\Delta H\#$ values and the large negative $\Delta S^{\#}$? values are compatible with (A) mechanism. Also the linear plots of k_{obs} vs. [R_2SnCl_2], [Ph_3SnCl] and the high span of k_2 values differing with the nature of the acceptors suggest an associative (A) mechanism.

The obtained trend shows that, k_2 values for reaction of [Co(campen)] is the least because of two electron withdrawing chlorides on the aromatic rings and two phenyl groups while [Co(amaen)] show the highest k_2 values because of two electron donating methyl groups. It is clear that the existence of methyl groups on the imine group make the Schiff base complexes better donors. In [Co(ampen)], however there is two electron withdrawing phenyl groups on the imine group that makes it a weaker donor compared with [Co(amaen)]. In [Co(appn)] there is one methyl group on the ethylene group which makes it a better donor compared with [Co(ampen)]. The presence of two chloride groups on the aromatic rings makes it a weaker donor compared with [Co(appn)]. Therefore the second order rate constants k_2 decrease according to the sequence:

[Co(amaen)] > [Co(appn)] > [Co(ampen)] > [Co(cappn)] > [Co(campen)].

CONCLUSIONS

The results of this work can be summarized as follow:

1. The relative Lewis acidities of different organotin(IV)chlorides toward a given

Co(™™) tetraaza Schiff base complex according to the k_2 values follow the trend: $Ph_2SnCl_2 > Me_2SnCl_2 > Bu_2SnCl_2 > Ph_3SnCl$.

2. The linear plots of k_{obs} vs. $[R_2SnCl_2]$, the high span of k_2 values and the large negative $DS^{\#}$? values suggest an associative (A) mechanism.
3. The kinetic parameters and the second order rate constants k_2 show the following trend of the donor properties of Co(™™) tetraaza Schiff base complexes toward a given acceptor:
[Co(amaen)] > [Co(appn)] > [Co(ampen)] > [Co(cappn)] > [Co(campen)].

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