

Preparation and Characterization of Tin(II) Complexes with Isomeric Series of Schiff Bases as Ligands

S. A. Sadeek[†] and M. S. Refat*

[†]Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt
Chemistry Department, Faculty of Education, Suez Canal University, Port-Said, Egypt
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[†]Chemistry Department, Faculty of Science, Zagazig University, Zagazig, Egypt
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요 약. N,N'-X-phenylenebis(acetylacetonimine) [X=ortho (L¹), meta(L²) 및 para(L³)]리간드를 갖는 주석(II) 화합물들을 합성하고, 그 특성을 원소분석, 적외선 분광광도법, 자외선/가시광선 분광광도법 및 열분석법을 이용하여 확인하였다. 자외선 분광광도법을 통하여, 주어진 ONNO 주계 리간드들의 이민(imine) 및 카보닐기의 배위 모드가 C_{2v} 대칭성을 갖는 것으로 나타났다. 또한 열분석 결과, Sn(L³) 화합물이 가장 높은 활성화 에너지를 가지는 반면, Sn(L²) 화합물이 가장 낮은 활성화 에너지를 가짐을 알 수 있었다.

주제어: Schiff base, Tin(II) complex, Acetylacetonate derivatives, Spectroscopy, Thermal property, Activation energy

ABSTRACT. Complexes of Sn(II) with L¹ = acac-*o*-phdnH₂ [N,N'-*o*-phenylene bis(acetylacetonimine)], L² = acac-*m*-phdnH₂ [N,N'-*m*-phenylene bis(acetylacetonimine)] and L³ = acac-*p*-phdnH₂ [N,N'-*p*-phenylene bis(acetylacetonimine)] have been prepared and characterized by elemental analyses, vibrational, electronic spectra and thermal studies (TGA and DTA). Vibrational spectra indicated the coordination mode of imine and carbonyl oxygen for ligands giving (ONNO) that belong to C_{2v} point group symmetry. The [Sn(L³)] complex has a maximum activation energy and [Sn(L²)] complex has a minimum activation energy.

Keywords: Schiff base, Tin(II) complex, Acetylacetonate derivatives, Spectroscopy, Thermal property, Activation energy

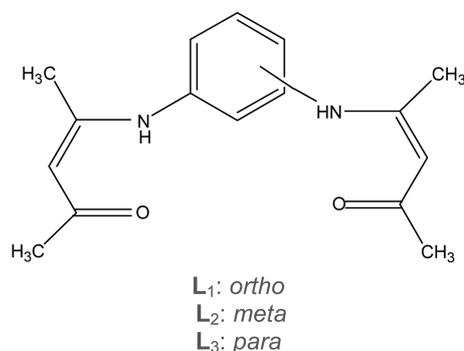
INTRODUCTION

Schiff base are capable of forming coordinate bonds with many of metal ions through both azomethine group and phenolic group or via its azomethine or phenolic groups.¹⁻³ Infrared spectroscopy has been widely used as a powerful means of distinguishing between the three possible donation sites of Schiff bases. A large number of Schiff bases and their

complexes are significant interest and attention because of their biological activity including anti-tumor, antibacterial, fungicidal and anti-carcinogenic properties.^{4,5} Tetradentate Schiff bases are well known to coordinate with various metal ions forming stable compounds, and some of these complexes are recognized as oxygen carriers.⁶

To continue our investigation in the field of Schiff base complexes,⁷⁻¹¹ we reported here preparation

and characterization of the new complexes $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$, $[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ and $[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$; ($\text{acac-}o\text{-phdnH}_2$ (L^1), $\text{acac-}m\text{-phdnH}_2$ (L^2) and $\text{acac-}p\text{-phdnH}_2$ (L^3) are $\text{N,N}'$ - o -phenylenebis(acetylacetonimine), $\text{N,N}'$ - m -phenylenebis(acetylacetonimine) and $\text{N,N}'$ - p -phenylenebis(acetylacetonimine), respectively). The solid products are well characterized through its elemental analysis, electronic spectra and thermal analysis, along with the assignment of their infrared spectra for most of the fundamental vibrations.



EXPERIMENTAL

All chemical used throughout this work were analytical reagent grade. The Schiff bases $\text{L}^1 = \text{acac-}o\text{-phdnH}_2$ [$\text{N,N}'$ - o -phenylene bis(acetylacetonimine)], $\text{L}^2 = \text{acac-}m\text{-phdnH}_2$ [$\text{N,N}'$ - m -phenylene bis(acetylacetonimine)] and $\text{L}^3 = \text{acac-}p\text{-phdnH}_2$ [$\text{N,N}'$ - p -phenylene bis(acetylacetonimine)] were prepared according to published method¹² from the condensation of o -phenylenediamine, m -phenylenediamine or p -phenylenediamine with acetylacetone in ethyl alcohol as a solvent. The separated precipitate was filtered, washed several times with minimum amount

of ethyl alcohol and dried under vacuum at room temperature. The isolated three Schiff bases were characterized through its infrared and elemental analysis. The deep pink solid complex $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$ was prepared from the addition of tin(II) chloride (4 mmol) in acetone to a stoichiometric amounts of the $\text{acac-}o\text{-phdnH}_2$, (1.088 g, 4 mmol) in acetone. The mixture was then stirred at room temperature for about 6-8 hrs. The separated solid product was filtered off, washed several times with acetone and dried under vacuum. The other two complexes $[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ (yellowish orange crystalline) and $[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$ (brownish black) were prepared in a similar way to that described above by the reaction of tin(II) chloride with $\text{acac-}m\text{-phdnH}_2$ and $\text{acac-}p\text{-phdnH}_2$, respectively. The complexes formed were characterized through their elemental analysis, infrared spectra as well as thermogravimetric (TG) and differential thermal analysis (DTA). Analysis of the products obtained is summarized in Table 1. The percentage of tin was determined using atomic absorption method. An atomic absorption spectrometer PYE-UNICAM SP 1900 fitted with a tin lamp was used for this purpose. The infrared spectra of the Schiff bases and tin(II) Schiff base complexes were recorded from KBr discs using a Perkin-Elmer 1430 ratio recording infrared spectrophotometer. Thermogravimetric (TG) and differential thermal analysis (DTA) of the Schiff base complexes $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$, $[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ and $[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$ were carried out using a Shimadzu computerized thermal analysis system DT-40. The system includes programs that process data from the analyzer with the chromatpac C-R 3A. The rate of heating of the samples was kept at 5°C min^{-1} . Accurate samples were analyzed under a

Table 1. The elemental analysis data

Complexes Elements	$[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$ $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Cl}_2\text{O}_2\text{Sn}$		$[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Cl}_2\text{O}_2\text{Sn}$		$[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$ $\text{C}_{16}\text{H}_{20}\text{N}_2\text{Cl}_2\text{O}_2\text{Sn}$	
	% Calc.	% Found	% Calc.	% Found	% Calc.	% Found
C	41.58	41.53	41.58	41.56	41.58	41.54
H	4.33	4.31	4.33	4.31	4.33	4.32
N	6.06	6.04	6.06	6.03	6.06	6.03
Cl	15.37	15.34	15.37	15.35	15.37	15.31
Sn	25.70	25.65	25.70	25.62	25.70	25.59

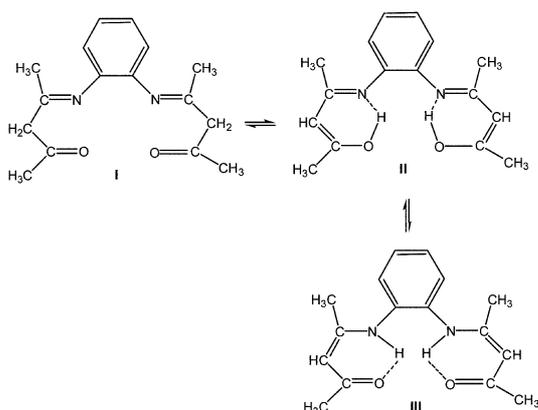
N_2 flow at 40 ml min^{-1} α -alumina powder was used as the DTA standard materials. Electronic spectra of the reactants and products were recorded at room temperature using Jenway 6405 Spectrophotometer with quartz cell of 1 cm path length.

RESULTS AND DISCUSSION

The three new complexes $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$, $[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ and $[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$ formed in the reaction of SnCl_2 with the Schiff bases $\text{acac-}o\text{-phdnH}_2$, $\text{acac-}m\text{-phdnH}_2$ and $\text{acac-}p\text{-phdnH}_2$ are characterized through their elemental analysis, infrared spectra and through their thermogravimetric investigation. The results enable us to characterize the complexes and make an assessment of the bonding and structures inherent in them.

The structural formula of these three complexes was obtained according to the following facts. Elemental analysis of the three complexes under investigation shows the presence of chloride ions in the three complexes. Solutions of these complexes react with silver nitrate giving a white precipitate of silver chloride indicating the existence of chloride in the ionic form i.e. outside the coordination sphere of the tin ion.

However, the Schiff bases under study may be present in tautomeric equilibrium (forms I-III), which resemble the forms given by Dudek and Holm¹³ for similar Schiff bases.



Distinction between the forms II and III is not large as a slight displacement of the hydrogen

nucleus. It has been concluded from infrared evidences that similar Schiff bases are largely tautomerized into II and III with appreciable amount of each existing in the solid state and in solution.^{13, 14}

Vibrational spectra

Infrared spectra of the Schiff bases under studies give a broad absorption band at about 3170 cm^{-1} , which may be due to the stretching vibration of either an O-H group in accordance with formula II or an N-H group of the type indicated by the formula III. Evidence of that¹⁴ is found in the broadening of this band and shift from normal positions ($3700\text{-}3400 \text{ cm}^{-1}$ for free O-H and $3400\text{-}3300 \text{ cm}^{-1}$ for free N-H). Also the free Schiff bases do not absorb in the region of carbonyl group, thus the formula I is eliminated and the ligand is believed to be a tautomeric equilibrium mixture of structures II and III.

The characteristic IR bands of $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$, $[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ and $[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$ are shown in Table 2. Before explaining such assignments, the structures of these complexes must first be discussed. Bottcher *et al.*¹⁶ reported the crystal structure of some related Schiff base complexes of Co(III) and indicated that the tetradentate Schiff base ligand (ONNO) coordinates the cobalt atom in a planar fashion with a slightly irregular tetragon with Co(III). The values of the Co-O and Co-N bond lengths in the equatorial ligand plane are 1.881 and 1.892 Å, respectively.

The complexes under investigations indicate that the tin(II) is only four coordinated and may take the structures shown in Scheme IV. With such structures the complexes may belong to C_{2v} symmetry and are expected to display 117 vibrational fundamental which are all monodegenerate. These are distributed between A_1 , A_2 , B_1 and B_2 motions; all are IR and Raman active, except for the A_2 modes, which are only Raman active.

In the spectra of the complexes, medium strong bands in the region $3340\text{-}3217 \text{ cm}^{-1}$ do exist, Fig. 1. These bands occur at lower frequency values known for O-H groups, therefore, the two bands found at 3279 and 3217 cm^{-1} for the complex $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$, and at 3320 , 3200 cm^{-1} for $[\text{Sn}(\text{acac-}$

Table 2. Infrared frequencies^(a) (cm⁻¹) and tentative assignments for (A): [Sn(acac-*o*-phdnH₂)]Cl₂, (B): [Sn(acac-*m*-phdnH₂)]Cl₂ and (C): [Sn(acac-*p*-phdnH₂)] Cl₂ complexes. complexes.

Frequencies, cm ⁻¹			Assignments ^(b)
(A)	(B)	(C)	
3279 m	3320 ms	3340 ms	ν _(N-H)
3217 m	3200 m		
3150 w, 3095 w	3080 vw, 3060 vw	3080 vw, 3060 vw	ν _(C-H) ; Phenyl
3080 w, 3050 w	3020 vw	3030 vw	
3020 w			
2960 w, 2915 w	2960 w, 2920 w	2970 w, 2920 w	ν _(C-H) ; =CH-, CH ₃
	2880 w	2860 w	
1630 s	1630 vs	1605 ms	ν _(C=O)
1590 s, 1557 w	1560 w, 1525 ms	1550 w, 1530 w	ν _(C=C)
1510 m	1500 ms, 1490 s	1505 w, 1495 w	
			Phenyl breathing modes
1476 m, 1425 s	1440 m, 1385 m	1475 sh, 1430 ms	-CH ₃ , CH-deformation
1385 s, 1357 m	1345 vw, 1335 w	1375 w, 1360 ms	
	1310 ms	1315 vs	
1271 m, 1244 m	1260 w, 1245 ms	1285 w, 1215 s	ν _(C-C) , ν _(C-O) , ν _(C-N)
1215 w, 1160 m	1200 m, 1155 m	1170 w, 1140 vw	
1110 m		1115 ms	
		1065 w, 1020 s	
1045 m, 1020 m	1030 m, 940 vw	950 m, 925 s	CH-bend; Phenyl, CH ₃
975 w, 952 w	890 w, 880 w	850 ms, 815 s	
884 w, 770 vs	845 ms, 775 w, 720 vw	800 w, 780 vw	
		755 ms, 733 ms	
656 w	675 w	690 w, 670 vw	CH- in-plane bend; Phenyl
628 mw	600 m	590 w	
514 mw	555 vw	550 w	ν _{as(Sn-O)}} ; O of Schiff base
475 w	490 w	505 ms	ν _{s(Sn-O)}} ; O of Schiff base
		480 w	
428 mw, 405 mw	410 vw, 400 vw	425 m	CH- out of plane bend
394 w, 366 mw		395 w	
345 s	325 vw	350 w	ν _{as(Sn-N)}} ; N of Schiff base
320 m	315 vw	330 vw	
295 m	300 w	290 w	ν _{s(Sn-N)}} ; N of Schiff base
265 s			

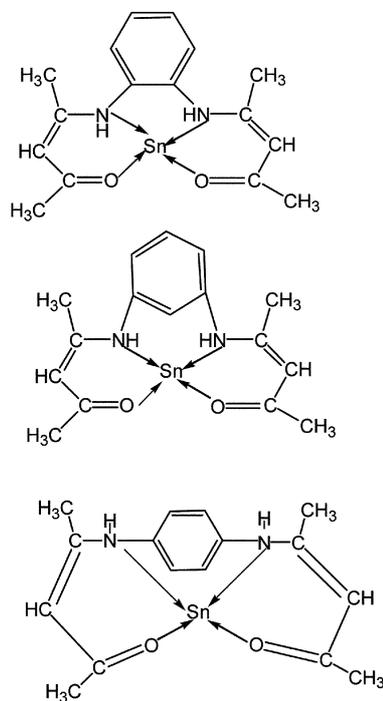
(a): s=strong, w=weak, m=medium, sh=shoulder, v=very, br = broad. (b): ν, stretching; δ, bending.

m-phdnH₂)]Cl₂ and 3340 cm⁻¹ for [Sn(acac-*p*-phdnH₂)]Cl₂ complexes, respectively, are assigned to coordinated N-H groups.¹⁵ Accordingly, the three complexes under study have coordinated N-H groups which indicated that, the Schiff bases under study coordinates with Sn(II) as a tetradentate through the two nitrogen and oxygen atoms as shown in Scheme IV and in the ketoamine form (III).

The ν (C-H) for the phenyl group are assigned in the region 3150-3020 cm⁻¹, Table 2, while those for the CH₃ and =CH- groups are shown as expected at

2970, 2960, 2915, 2880 and 2860 cm⁻¹. The carbonyl bands ν (C=O) of our complexes are shown at 1630 and 1605 cm⁻¹ as a strong and medium strong band. The ν (C=C) stretching vibrations and phenyl breathing modes of the three complexes are observed in the range 1590-1490 cm⁻¹. The bending vibrations, δ(-CH₃) and (=CH) are observed in the region 1476-1310 cm⁻¹. The description of their assignments follow the expression developed and used by others.^{17,18}

The stretching vibrations of ν (C-O), ν (C-C) and



Scheme IV

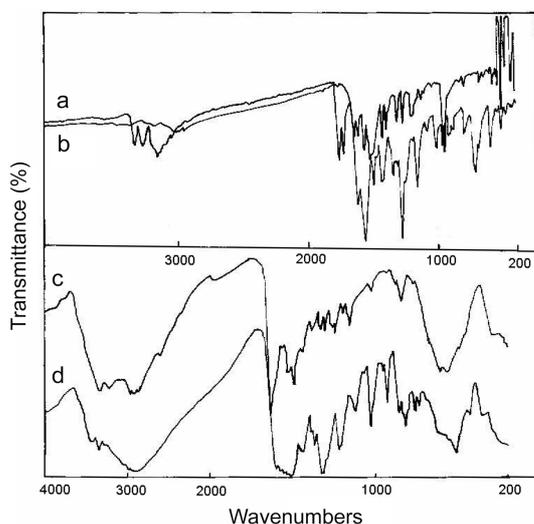


Fig. 1. Infrared spectra of (a): acac-*o*-phdnH₂ Schiff base, (b): [Sn(acac-*o*-phdnH₂)]Cl₂, (c): [Sn(acac-*m*-phdnH₂)]Cl₂ and (d): [Sn(acac-*p*-phdnH₂)]Cl₂ complexes.

ν (C-N) occur in the region 1285-1110 cm⁻¹, Table 2. The tin-oxygen (O of Schiff base) stretching vibration, ν_{as} (Sn-O) are assigned for the three complexes at

514, 555 and 550 cm⁻¹, while the corresponding ν_s (Sn-O) are assigned at 475, 490 and 505, 480 cm⁻¹ for *o*-, *m*- and *p*- Schiff base complexes, respectively. The ν_{as} (Sn-N) are assigned at 345, 320 cm⁻¹ and 325, 315 cm⁻¹ and 350, 330 cm⁻¹, for our study complexes, while ν_s (Sn-N) are assigned to the strong and weak infrared bands around 295 cm⁻¹. The assignments of these metal-ligand stretches are made on the basis of their activities as well as the relative bond strengths shown from the crystal structure data known¹⁶ for some related Schiff base complexes, and also that the assigned bonds do not exist in the free ligand spectra. However, the ν (Sn-N) stretches were assigned at relatively low frequency values compared to ν (Sn-O). This is in agreement with the bond length values, which indicate that the Sn-N bond is the weakest with a large value of bond length.

Thermal studies

Differential thermal analysis (DTA) and thermogravimetric (TG) were measured for the three complexes to investigate the mode of decomposition of these types of complexes, Fig. 2. The maximum temperature values $T_{max}/^{\circ}\text{C}$ together with the corresponding weight loss for each step of the decomposition are recorded in Table 3. The decomposition of the complex [Sn(acac-*o*-phdnH₂)]Cl₂ falls in one degradation stage. This stage of decomposition appears at two maxima 120 and 165 °C is associated with a weight loss of 54.96% corresponding to the loss of 5C₂H₂+2HCl+2NH₃+H₂O. The weight loss in this stage 54.96% is in full agreement with the calculated value of 55.23%. The thermal degradation for the other two complexes, [Sn(acac-*m*-phdnH₂)]Cl₂ and [Sn(acac-*p*-phdnH₂)]Cl₂, exhibit approximately one main decomposition step, Fig. 2, this stage of decomposition occurs at maximum temperatures 141, 259 and 109, 153 °C, respectively, and accompanied by a weight loss of 47.11 and 66.16% correspond to the loss of 3C₂H₄+2HCl+2NH₃+CO and 7C₂H₂+2HCl+N₂+H₂O+H₂ in agreement with our predicted weight loss of 47.44 and 65.63% for [Sn(acac-*m*-phdnH₂)]Cl₂ and [Sn(acac-*p*-phdnH₂)]Cl₂ complexes, respectively. The above going conclu-

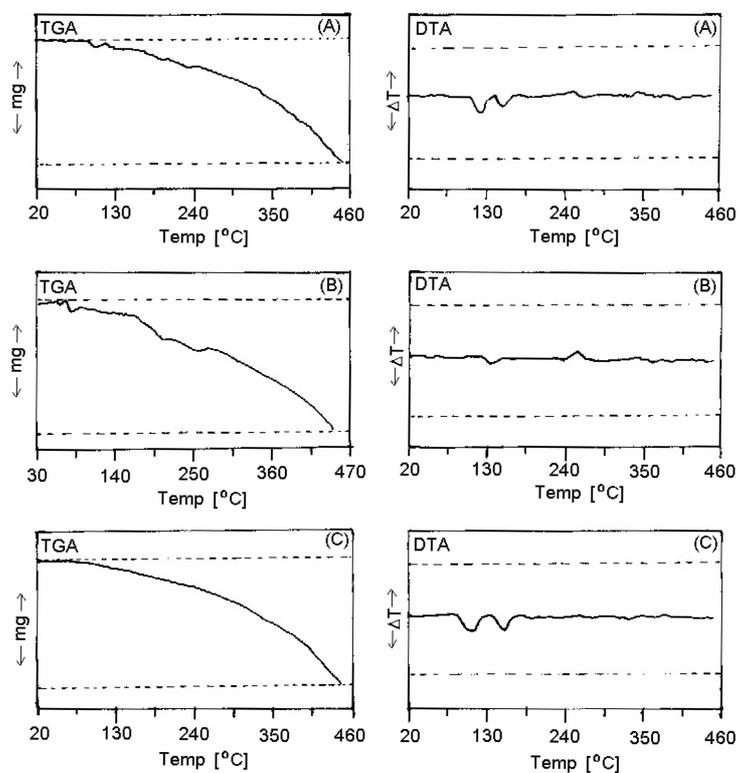


Fig. 2. TGA and DTA curves of (A): $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$, (B): $[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ and (C): $[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$ complexes.

Table 3. The maximum temperature, $T_{\text{max}}/^\circ\text{C}$, and weight loss values of the decomposition stages for the $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$, $[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ and $[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$ complexes.

Complexes	Decomposition	$T_{\text{max}}/^\circ\text{C}$	Lost species	%Weight losses	
				Found	Calc.
$[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$	First stage	120 °C	$5\text{C}_2\text{H}_2$	54.96%	55.23%
		165 °C	2HCl 2NH_3 H_2O		
	Total loss		54.96%	55.23%	
	Residue		45.04%	44.77%	
$[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$	First stage	141 °C	$3\text{C}_2\text{H}_4$	47.11%	47.44%
		259 °C	2HCl 2NH_3 CO		
	Total loss		47.11%	47.44%	
	Residue		52.89%	52.56%	
$[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$	First stage	109 °C	$7\text{C}_2\text{H}_2$	66.16%	65.63%
		153 °C	2HCl N_2 H_2O H_2		
	Total loss		66.16%	65.63%	
	Residue		33.84%	34.37%	

sion was also supported by the fact that the infrared spectra of the final decomposition products for the complexes under investigation shows the absence of all bands associated with the Schiff base ligands and instead the characteristic spectrum of SnO is appeared. Accordingly, the following mechanisms are proposed for the thermal decomposition of the Schiff base complexes as follows:

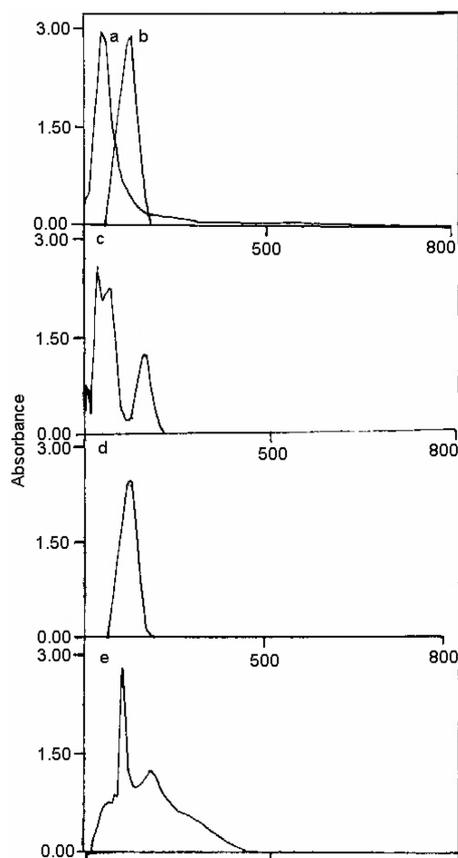
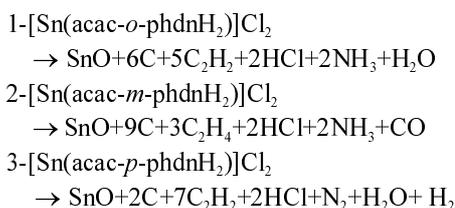


Fig. 3. Electronic spectra of (a): SnCl_2 , (b): Acetylacetonate, (c): $\text{acac-}o\text{-phdnH}_2$, (d): $\text{acac+}o\text{-phenylenediamine}$, (e): $\text{Acetylacetonate+}o\text{-phenylenediamine / SnCl}_2$ complex.

Electronic spectra

The electronic spectra of the SnCl_2 , acetylacetonate, schiff base (e.g. $\text{acac-}o\text{-phdnH}_2$) and the complex, $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$ have been measured in methanol as a solvent, Fig. 3. The spectra of the uncomplexed ligand ($\text{acac-}o\text{-phdnH}_2$) show a characteristic band at 275 nm which is assigned to $n \rightarrow \pi^*$ transition to the chromophoric $\text{C}=\text{O}$ group. This band shows a bathochromic shift in the tin(II) complexes of all the ligands. This is attributed to the involvement of carbonyl group in metal complexation as indicated by IR studies. The Schiff bases, $\text{acac-}o\text{-phdnH}_2$, $\text{acac-}m\text{-phdnH}_2$ and $\text{acac-}p\text{-phdnH}_2$ were prepared in this study play a role of donor type (n -donor). The n -donor is neutral, even systems containing relatively an easily ionized atomic lone pair of electrons.¹⁹ The donated electrons come from a non-bonding molecular orbital occupied in the original donor by a lone pair of electrons as follows:



On the other side tin(II) chloride reacted as a vacant orbital acceptor¹⁹ which is neutral even system or even ions in which an orbital or orbitals of relatively high electron affinity are vacant. This type of acceptors combine especially with n -donors to form fairly stable compounds by partial dative acceptance of electron into vacant orbital as follows:



To make a comparison between reactants and products (Fig. 3), there are three electronic spectra bands observed around 260 and 310 nm due to $\pi \rightarrow \pi^*$ of acetylacetonate ring ($\text{C}=\text{O}$) and at around 379 nm as shoulder broad peak due to the metal-to-ligand charge transfer transition,²⁰ between Schiff bases and SnCl_2 (the color of schiff base widely change as soon as tin(II) chloride added from brownish yellow to pink color).

Kinetic calculation

From TGA curves, the order (n), activation energy ($E^*/\text{kJ mol}^{-1}$), and the pre-exponential factor, Z , for thermal reactions of the complexes have been elucidated by linearisation method of Horowitz-Metzger

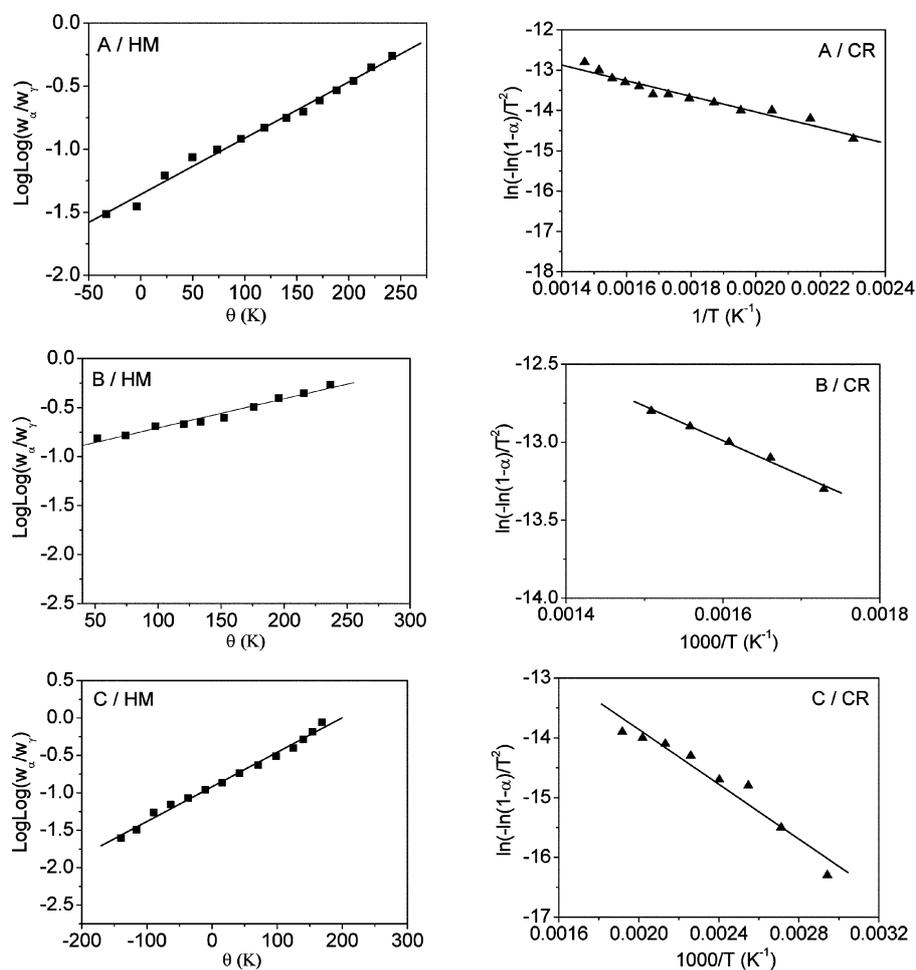


Fig. 4. Kinetic parameter of (A): $[\text{Sn}(\text{acac-}o\text{-phdnH}_2)]\text{Cl}_2$, (B): $[\text{Sn}(\text{acac-}m\text{-phdnH}_2)]\text{Cl}_2$ and (C): $[\text{Sn}(\text{acac-}p\text{-phdnH}_2)]\text{Cl}_2$ complexes using Horowitz-Metzger (HM) approximation method and Coats-Redfern (CR) integral method.

Table 4. Kinetic parameters determined using the Coats-Redfern (CR) and Horowitz-Metzger (HM).

Complex	Horowitz-Metzger					Coats-Redfern					n
	E/ kJmol ⁻¹	Z/ s ⁻¹	ΔS / Jmol ⁻¹ K ⁻¹	ΔH / kJmol ⁻¹	ΔG / kJmol ⁻¹	E/ kJmol ⁻¹	Z/ s ⁻¹	ΔS / Jmol ⁻¹ K ⁻¹	ΔH / kJmol ⁻¹	ΔG / kJmol ⁻¹	
L1	16.4	2.28 E-1	-260	12.7	127	16.1	1.25E+7	-254	12.5	122.6	1
L2	10.4	3.20 E-2	-277	6.82	125	10.5	6.94 E+ 6	-265	6.2	120.8	1
L3	25.1	7.65 E-1	-252	20.6	155	24.6	6.13E+ 6	-220	19.6	149	1

(HM) approximation method and Coats-Redfern integral method.^{21,22} The entropy of activation ΔS^* in (JK⁻¹mol⁻¹) was calculated by using the equation: $\Delta S^* = R \ln(Ah/k_B T_s)$, where k_B is the Boltzmann constant, h is the Plank's constant and T_s is the DTA peak temperature.²³

The enthalpy activation, ΔH^* , and Gibbs free energy, ΔG^* , were calculated from; $\Delta H^* = E^* - RT$ and $\Delta G^* = \Delta H^* - T \Delta S^*$, respectively. The data is presented in Fig. 4 and Table 4. The complexes with all the ligands start decomposing in the range 382-583 K. This shows that the complexes are anhydrous. All

complexes decomposed via first order kinetics and energy of activation is 16-25 kJmol⁻¹. The order of activation energy is: L³>L¹>L² for tin(II) complexes. The literatures contain various explanations of the relative order of thermal stability of complexes.²⁴⁻²⁶ The final product of the decomposition in all the complexes is SnO as confirmed by experimental and calculated weight losses.

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