

## Organotin(IV) Complexes of Some 2-Pyrazoline Derivatives, Part (II): $\text{PhSnCl}_3$ and $\text{SnCl}_4$ Complexes

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The reactions of  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  with 2-pyrazoline derivatives (L) in a 1 : 1 molar ratio have been described. The complexes  $\text{PhSnCl}_3 \cdot \text{L}$  and  $\text{PhSnCl}_4 \cdot \text{L}$  have been identified by C,H,N elemental analyses, IR and NMR spectroscopy. The spectral data of some of the complexes formed show that the 2-pyrazoline derivative is tautomerized, during the reaction, to the most stable hydrazone form and the later coordinates with tin compounds via N-N linkage and not via N2 and CO sites of the hydrazone. This has been confirmed by preparing some chroman-4-one complexes of  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  and comparing their IR spectra with those of hydrazone ones. Almost all the complexes prepared show some 1 : 1 conductivity in both solvents, acetonitrile and DMF, indicating the presence of ionic species  $[\text{PhSn}(\text{L})\text{Cl}_2]\text{Cl}$  and  $[\text{Sn}(\text{L})\text{Cl}_3]\text{Cl}$ .

### INTRODUCTION

In part I of this work, we have given a brief survey about organotin complexes, with some oxygen, sulphur and nitrogen containing ligands, and about their biological importance<sup>1</sup>. In the present part, we are presenting the results obtained from the reaction of 2-pyrazoline derivatives with  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  as very strong Lewis acids compared to  $\text{R}_3\text{SnCl}$  and  $\text{R}_2\text{SnCl}_2$  of part I of this work.

### EXPERIMENTAL

The <sup>1</sup>H NMR spectra were recorded at Basrah University, Basrah, Iraq, on a Jeol, JNM-EX-90 FT NMR, using  $\text{CDCl}_3$  as a solvent with TMS as an internal standard. IR spectra were recorded on Perkin-Elmer 580 B infrared spectrophotometer in the range 4000–200  $\text{cm}^{-1}$  using Nujol Mull and CsI discs. Analyses of the complexes were carried out at the College of Science, University of Mosul, Iraq, using a CHN analyser, Type 1106 (Carlo Erba). Electronic spectra were recorded on a UV/Vis spectrophotometer, model 160 Shimadzu Koyoto (Japan),

For part I of this work, see reference 1.

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using DMF as a solvent and quartz cell of 1 cm width. Conductivity measurements were done for  $10^{-3}$  M solutions of the complexes in DMF and  $\text{CH}_3\text{CN}$  at room temperature ( $25^\circ\text{C}$ ), using a conductivity meter, model 4070 (Jenway).

The compound  $\text{SnCl}_4$  was a commercial product (Fluka). The compound  $\text{PhSnCl}_3$  was prepared by a standard method<sup>2,3</sup>.

The ligands, chroman-4-one and 2-pyrazoline derivatives (I and IIa-j) were prepared as described in part I of this work<sup>1</sup>.

### Preparation of the complexes $\text{PhSnCl}_3\cdot\text{L}$ and $\text{SnCl}_4\cdot\text{L}$

The ligand, 2-pyrazoline derivative (LII) (0.5 mmol), was dissolved in an organic solvent,  $\text{CHCl}_3$  or EtOH or acetone (5 mL), according to its solubility. To this was added a solution of the tin compound (0.5 mmol) in the corresponding solvent (5 mL) with vigorous stirring. The resulting solution was evaporated to *ca.* 1/2 its original volume, then petroleum spirit ( $40\text{--}60^\circ\text{C}$ ) was added to the point of turbidity and the mixture was kept in the refrigerator for several hours. The resulting crystalline product was filtered, washed several times with pet. spirit and dried under vacuum for several hours.

When the product was an oil, it was separated from the mother liquor by decantation, washed with light petroleum, and dried. The oil could be solidified when stirred with light petroleum overnight. The yield of the complexes  $\text{PhSnCl}_3\cdot\text{L}$  and  $\text{SnCl}_4\cdot\text{L}$  ranged between 70 and 90%.

## RESULTS AND DISCUSSION

The physical properties of  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  complexes of 2-pyrazoline derivatives are listed in Table-1 and the  $^1\text{H}$  NMR spectral data of some selected complexes are listed in Table-2. The elemental composition of the complexes prepared corresponds to 1 : 1 (tin : ligand) molar ratio, *i.e.*,  $\text{Ph}_3\text{SnCl}\cdot\text{L}$  and  $\text{SnCl}_4\cdot\text{L}$ .

### Spectral data and structure

IR and  $^1\text{H}$  NMR spectra of the  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  complexes of 2-pyrazoline derivatives were recorded for establishing the mode of bonding.

We have reported in part I of this work that  $\text{R}_3\text{SnCl}$  and  $\text{R}_2\text{SnCl}_2$  can coordinate with 2-pyrazoline derivatives to give 5- and 6-coordinated complexes, respectively.

In the present work, the tin compounds used, *i.e.*,  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  have a great tendency (strong Lewis acids) to coordinate with 2-pyrazoline derivatives (LII) to form the complexes  $\text{PhSnCl}_3\cdot\text{L}$  and  $\text{SnCl}_4\cdot\text{L}$  with tin of hexa-coordination number.

With a few exceptions (*vide infra*) the coordination of  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  with this type of ligands takes place, usually, via N2-OH linkage as shown by the IR spectral measurements.



Ligand L (II)*	Complex	Colour	m.p. (°C)	Analyses: Found (Calc.) %				Selected IR bands (cm <sup>-1</sup> )†				UV/Vis $\lambda_{\text{max}}$ ( $\Sigma_{\text{max}}$ )	Conductivity ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>		
				C	H	N		v(C≡N) ( $\Delta\nu$ )	v(Sn-O)	v(Sn-N)	v(Sn-Cl)			v(Sn-C)	DMF
d	—	off-white	132-134	—	—	—	—	1600 m, sh	—	—	—	—	232, 276, 318	—	—
	PhSnCl <sub>3</sub> .IIId	orange	212-214	43.4 (43.9)	4.6 (4.4)	5.3 (5.4)	—	1590 s, b (-10)	422 m	439 s	302 s, b	272 m	281(7230), 340(6780)	33	86
e	SnCl <sub>4</sub> .IIId	yellow	188-191	32.4 (32.6)	3.8 (3.8)	5.60 (5.85)	—	1573 s (-27)	405 w	435 m	294 s, b	—	231(1450), 272(6650), 329(4650)	58	70
	—	yellow	100-101	—	—	—	—	1605 m, sh	—	—	—	—	232, 282, 345	—	—
f	SnCl <sub>4</sub> .IIe	brown	230-232	32.55 (32.60)	3.8 (3.8)	5.70 (5.85)	—	1591 s (-14)	415 m	449 s, b	319 s	—	230(3690), 255(2530), 335(17260)	49	40
	—	white	103-105	—	—	—	—	1600 s	—	—	—	—	230, 268, 328	—	—
g	PhSnCl <sub>3</sub> .IIId	yellow	210-212	44.0 (43.9)	4.55 (4.40)	5.2 (5.4)	—	1560 s (-40)	398 m	429 m	302 s	241 m	340(6990), 370(21320)	35	87
	SnCl <sub>4</sub> .IIIf	yellow	66-68	32.5 (32.6)	3.7 (3.8)	5.60 (5.85)	—	1570 s, sh (-30)	401 m	429 m	306 s, b	—	231(1730), 273(9770), 324(5840)	52	81
g	—	brown	118-120	—	—	—	—	156 s, sh	—	—	—	—	230, 278, 336	—	—
	SnCl <sub>4</sub> .IIg	brown	180-182	30.2 (30.0)	3.4 (3.3)	5.6 (5.8)	—	1585 m (-11)	408 w	432 m	280, 306 s	—	230(1750), 275(8030), 345(16090)	41	43

Ligand L (II)*	Complex	Colour	m.p. (°C)	Analyses: Found (Calc.) %				Selected IR bands (cm <sup>-1</sup> )†				UV/Vis $\lambda_{\text{max}}$ ( $\Sigma_{\text{max}}$ )	Conductivity ohm <sup>-1</sup> cm <sup>2</sup> mol <sup>-1</sup>	
				C	H	N	v(C=N) ( $\Delta\nu$ )	v(Sn-O)	v(Sn-N)	v(Sn-Cl)	v(Sn-C)		DMF	CH <sub>3</sub> CN
h	PhSnCl <sub>3</sub> ·IIh	yellow	124-125	—	—	—	1600 m	—	—	—	230, 285	—	—	
		yellow	168-170	41.1 (41.3)	4.3 (4.2)	4.9 (5.1)	1578 m (-22)	391 w (-22)	425 m	276 s	251 w (-22)	238(940), 280(15580)	65	83
i	PhSnCl <sub>3</sub> ·IIi	yellow	206-208	—	—	—	1595 s	—	—	—	230, 279, 345	—	—	
		orange	134-137	40.9 (41.25)	4.3 (4.3)	4.6 (4.8)	1578 s (-17)	398 w (-17)	425 s	285 s, b	251 m	284(6880), 365(20200)	50	82
j	PhSnCl <sub>3</sub> ·IIIj‡	orange	134-136	30.8 (30.1)	3.8 (3.7)	5.0 (5.2)	1578 s (-17)	415 m (-17)	422 m	293 s	—	232(4210), 380(24610)	43	68
		yellow	100-101	—	—	—	1605 s, b	—	—	—	—	237, 276, 364	—	—
j	SnCl <sub>4</sub> ·IIIj‡	yellow	194-196	41.1 (41.65)	3.3 (3.5)	5.3 (5.7)	1580 s (-25)	—	444 m	290 s, b	267 w	280(19230), 351(6950)	31	70
		brown	168-170	30.2 (29.45)	2.8 (2.7)	6.0 (6.2)	1585 s (-20)	—	446 m	290 s, b	—	230(1720), 276(11520), 367(21930)	31	79

\*For the ligands IIa-j, see part I of this work.<sup>1</sup>†In Nujol Mulls: s, strong; m, medium; w, weak; sh, shoulder and b, broad bands. ( $\Delta\nu$ ) values were measured as  $\nu_{\text{complex}} - \nu_{\text{ligand}}$ .‡Complexes gave a strong IR band at 1667, 1668, 1680 and 1663 cm<sup>-1</sup>, respectively, attributed to uncoordinated CO group of the hydrazone tautomer (Scheme-1).

TABLE-2

<sup>1</sup>H NMR data\*, δ(ppm) AND J(Hz) FOR SELECTED PhSnCl<sub>3</sub>-L AND SnCl<sub>4</sub>-L COMPLEXES OF 2-PYRAZOLINE DERIVATIVES

Complex	δ(Ph-Sn)	Ligand assignments					
		δ(CH <sub>3</sub> C-5)	δ(HC-4)	δ(HC-5)	δ(R <sub>3</sub> -H)	δ(Ar-H)	δ(H-N)
SnCl <sub>4</sub> -IIIb	—	1.6 J = 7.0	3.7 b	4.5 b	2.25 s, 6H(CH <sub>3</sub> ) <sub>2</sub>	7.8 s, HC-3' 6.8 s, HC-6'	5.7 b
PhSnCl <sub>3</sub> -IIc	7.4- 7.8 m	1.45 d J = 0.7	2.7 dd	4.15 m	3.8 s, 3H(OCH <sub>3</sub> ) 3.9 s, 3H(OCH <sub>3</sub> )	6.45 s, HC-3' 7.2 s, HC-6'	5.9 b
SnCl <sub>4</sub> -IIIc	—	1.6 d J = 0.7	2.65 dd	4.51 m	3.95 s, 6H(OCH <sub>3</sub> ) <sub>2</sub>	7.45 s, HC-3' 6.45 s, HC-6'	5.6 b
SnCl <sub>4</sub> -IIe	—	1.5 s	2.7 s	—	2.2 s, 3H(CH <sub>3</sub> ) 2.3 s, 3H(CH <sub>3</sub> )	6.7 b, HC-4' 7.75 b, HC-6'	5.1 b

\*Downfield from internal TMS using CDCl<sub>3</sub> as a solvent: s, singlet; d, doublet; dd, doublet of doublets; m, multiplet and b, broad signals.

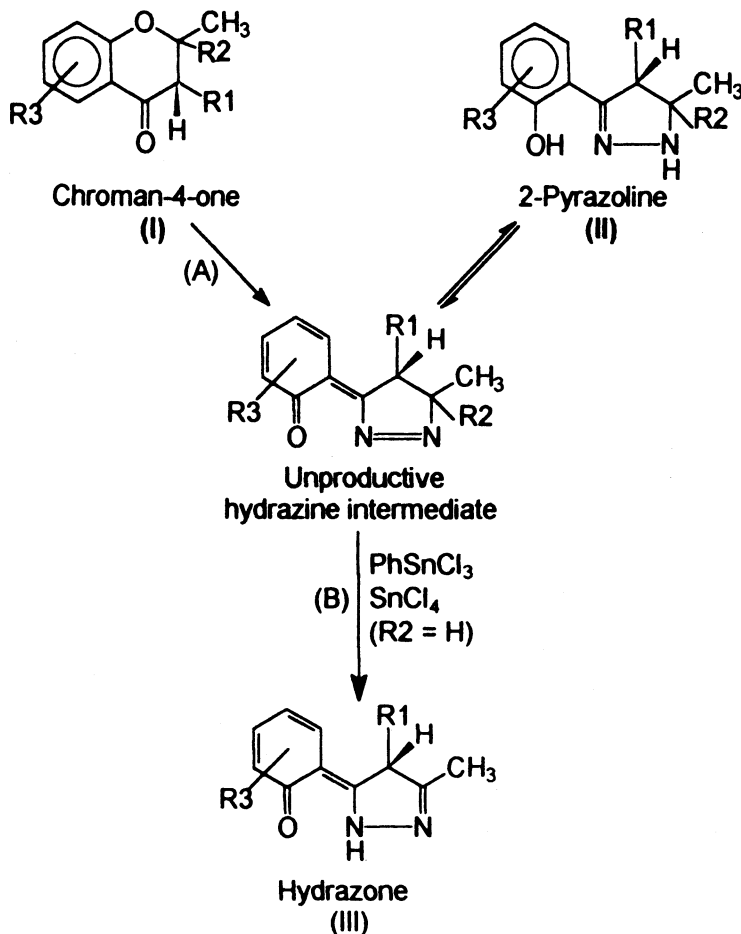


TABLE-3  
PHYSICAL PROPERTIES OF THE NEW CHROMAN-4-ONE DERIVATIVES AND THEIR TIN COMPLEXES

Ligand* L(I)	Complex	Colour	m.p.(°C)	Analyses: Found (Calc.) %			Selected IR data (cm <sup>-1</sup> )		UV/Vis $\lambda_{\text{max}}$ (nm)
				C	H		$\delta(\text{CO})$	$\delta(\text{Sn-Cl})$	
Ik. R1 = H, R2 = CH <sub>3</sub> , R3 = 5,7-(CH <sub>3</sub> ) <sub>2</sub>		yellow	55-57	76.1 (67.5)	7.5 (7.8)		1676 s	—	233, 268.5, 323.5
	PhSnCl <sub>3</sub> Ik	white	138-140	53.8 (54.1)	5.0 (5.2)		1640 s	285 s, b	255, 299, 323
Il. R1 = CH <sub>3</sub> , R2 = H, R3 = 5,8-(CH <sub>3</sub> ) <sub>2</sub>		yellow-brown	142-144	76.3 (76.5)	7.6 (7.8)		1667 s	—	232, 278, 335.5
	SnCl <sub>4</sub> Il	yellow	178-180	46.5 (46.7)	4.4 (4.8)		1630 s	278 s, b	271, 421.5
Im. R1 = CH <sub>3</sub> , R2 = H, R3 = 6,7-(CH <sub>3</sub> ) <sub>2</sub>		yellow	70-72	76.5 (76.5)	7.7 (7.8)		1667 s	—	232.5, 268, 324
	PhSnCl <sub>3</sub> Im	green-yellow	280-282	53.9 (54.1)	5.1 (5.2)		1635 s	297 s, b	235.5, 269.5, 324.5
In. R1 = CH <sub>3</sub> , R2 = H, R3 = 6,7-(CH <sub>3</sub> ) <sub>2</sub>		white	140-143	66.0 (66.1)	6.4 (6.8)		1662 s	—	238.5, 272.5, 331.5
	PhSnCl <sub>3</sub> In	white	132-134	49.2 (49.6)	4.5 (4.8)		1640 s	272 s, b	338, 350.5

\*For the ligands Ia-j, see part I of this work<sup>1</sup>.

The routine IR spectral measurements clearly showed that coordination of tin compounds with these ligands had taken place. The IR bands appearing in the regions 430–350 and 450–410  $\text{cm}^{-1}$  are tentatively assigned to  $\nu(\text{Sn—O})$  and  $\nu(\text{Sn—N})$ , respectively, which serve as good indicators of coordination via O and N donor sites<sup>1</sup>. It is more likely that N2 rather than N1 site of the 2-pyrazoline derivatives has been involved in the coordination with tin compounds, and this was supported by the drastic decrease ( $\Delta\nu = 10\text{--}35 \text{ cm}^{-1}$ ) in the  $\nu(\text{C=N})$  value (Table-1) on going from the free ligand to its complex<sup>1,4,5</sup>. It is then concluded that  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  coordinate with 2-pyrazoline derivatives via N2–OH linkage to form six-member chelate rings. However, in few cases, where the ligand (L) is IIb, IIc and IIj, the coordination of  $\text{SnCl}_4$ , with the three ligands, and  $\text{PhSnCl}_3$ , with the third one only, is surprisingly shown to take another route, in which a clear and strong band in the region 1680–1663  $\text{cm}^{-1}$  appears, which is assigned to uncoordinated  $\nu(\text{C=O})$ . Since 2-pyrazoline derivatives contain no carbonyl group in its structure<sup>1</sup>, therefore, a tautomerization of 2-pyrazoline must have taken place, during the coordination with the strong Lewis acids  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$ , to the most stable hydrazone structure<sup>6</sup>, possibly via an unproductive hydrazine intermediate. The latter was suggested as the last step in the proposed mechanism for formation of 2-pyrazoline derivatives from the corresponding chroman-4-one derivatives<sup>7</sup> (Scheme-1).

Furthermore, the coordination of  $\text{PhSnCl}_3$  or  $\text{SnCl}_4$  with hydrazone occurs most possibly via the N–N linkage and not via the N–O linkage, *i.e.*, C=O group did not involve in the coordination.

This was achieved, mainly, by  $\nu(\text{C=O})$  values of the so formed complexes,  $\text{SnCl}_4\cdot\text{IIb}$ ,  $\text{SnCl}_4\cdot\text{IIc}$ ,  $\text{PhSnCl}_4\cdot\text{IIj}$  and  $\text{SnCl}_4\cdot\text{IIj}$ , which range between 1680 to 1663  $\text{cm}^{-1}$ , frequencies for non-coordinated carbonyl groups.

In order to examine this point more precisely, a reaction of  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  with some new chroman-4-one derivatives (as containing carbonyl group), other than those mentioned in part I of this work<sup>1</sup> and not reported previously<sup>7</sup>, was carried out as mentioned in the experimental part for the preparation of 2-pyrazoline derivatives. The physical properties of the new chroman-4-one derivatives and their  $\text{PhSnCl}_3$  and  $\text{SnCl}_4$  complexes are listed in Table 3, and their <sup>1</sup>H NMR spectra are listed in Table 4.

TABLE-4

<sup>1</sup>H NMR DATA,  $\delta$ (PPM) AND  $J(\text{H}_2)$  FOR THE NEW CHROMAN-4-ONE DERIVATIVES AND ONE  $\text{PhSnCl}_3\cdot\text{L}$  COMPLEX

Ligand L(I)	$\delta(\text{CH}_3\text{C-2})$	$\delta(\text{HC-3})$	$\delta\text{R}_1$	$\delta\text{R}_2$	$\delta\text{R}_3$	$\delta(\text{Ar-H})$
Ik	1.4 s (3H)	2.65 s (2H)	1.4 s (3H)	2.3 s ( $\text{CH}_3\text{C-7}$ ) 2.6 s ( $\text{CH}_3\text{C-5}$ )	6.6 b (2H)	
II	1.5 m (3H)	3.65 m (1H)	1.5 m (3H)	3.1 m (1H)	2.4 s ( $\text{CH}_3\text{C-8}$ ) 2.7 s ( $\text{CH}_3\text{C-5}$ )	6.9 b (2H)
In	1.5 d (3H) $J = 6.4$	4.2 m (1H)	1.2 d (3H) $J = 6.4$	2.5 m (1H)	3.85 s ( $\text{CH}_3\text{OC-7}$ ) 3.9 s ( $\text{CH}_3\text{OC-6}$ )	6.4 b (2H)
$\text{PhSnCl}_3\cdot\text{In}$	1.4 d (3H) $J = 6.5$	4.2 m (1H)	1.2 d (3H) $J = 6.5$	2.5 m (1H)	3.8 s ( $\text{CH}_3\text{OC-7}$ ) 3.9 s ( $\text{CH}_3\text{OC-6}$ )	6.4 b (2H) 7.6 b (5H)



The stretching frequency of CO group of the free chroman-4-one was significantly decreased ( $\Delta\nu = 22\text{--}37\text{ cm}^{-1}$ ) upon coordination with tin compounds. This clearly means that tin compounds had been linked with chroman-4-one derivatives via C=O group, in contrast to the coordination of hydrazone derivatives (Scheme-1) with tin compounds, in which CO group does not involve in the coordination with tin. This may be due to the fact that hydrazone derivatives have an alternative coordination site, *i.e.*, N-N linkage, in addition to CO group, available to bound with tin.

The NMR spectral data of the free chroman-4-one and 2-pyrazoline derivatives were extensively discussed in our previous work<sup>7</sup>. The <sup>1</sup>H NMR spectra of some have been selected complexes of 2-pyrazoline, hydrazone and chroman-4-one derivatives were recorded in CDCl<sub>3</sub>. The spectral data of the complexes showed no significant differences from those of the free ligands.

### Electronic spectra

UV/Vis spectral data for the complexes PhSnCl<sub>3</sub>·L and SnCl<sub>4</sub>·L (Tables 1 and 3) showed absorption bands almost certainly similar to those of the complexes R<sub>3</sub>SnCl·L and R<sub>2</sub>SnCl<sub>2</sub>·L discussed in part (I) of this work.

### Conductivity measurements

The conductivity measurements for 10<sup>-3</sup> molar solutions of both complexes PhSnCl<sub>3</sub>·L and SnCl<sub>4</sub>·L at room temperature in both solvents acetonitrile and DMF fall in the range 34–118 and 31–65 ohm<sup>-1</sup> cm<sup>2</sup> mol<sup>-1</sup>, respectively. These figures assigned to some 1 : 1 conductive species in both solvents<sup>8</sup>, *i.e.*, the ionic complexes [PhSn(L)Cl<sub>2</sub>] Cl and [Sn(L)Cl<sub>3</sub>]Cl, respectively.

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