

# Thermochemistry of adducts of tin(IV) chloride with amides and thioamides

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## Abstract

The compounds  $[\text{SnCl}_4(\text{L})_2]$  (where L is urea (u), 1,1-dimethylurea (1,1-dmu), 1,3-dimethylurea (1,3-dmu), tetramethylurea (tmu), thiourea (tu), tetramethylthiourea (tmtu) or 1-allyl-2-thiourea (atu)) were synthesized and characterized by melting points, elemental analysis, thermal studies and IR spectroscopy. The enthalpies of dissolution of the adducts, tin(IV) chloride and ligands in methanol were measured and by using thermochemical cycles the following thermochemical parameters for the adducts, have been determined: the standard enthalpies for the Lewis acid/base reactions ( $\Delta_r H^\theta$ ), the standard enthalpies of formation ( $\Delta_f H^\theta$ ), the standard enthalpies of decomposition ( $\Delta_D H^\theta$ ), the lattice standard enthalpies ( $\Delta_M H^\theta$ ) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ( $\Delta_r H^\theta(\text{g})$ ). The mean standard enthalpies of the tin-oxygen ( $\bar{D}(\text{Sn}-\text{O})$ ) and tin-sulphur ( $\bar{D}(\text{Sn}-\text{S})$ ) bonds have been estimated. © 2000 Elsevier Science B.V. All rights reserved.

*Keywords:* Tin(IV); Tin(IV) chloride; Sn–O and Sn–S bonds; Thermochemical parameters; Thermochemistry

## 1. Introduction

Adducts of tin(IV) halides with amides and thioamides are reported in the literature [1–5]. Their preparation and characterization are described in those articles. However, no information about the enthalpies of the tin-oxygen and tin-sulphur bonds in these compounds is available. Adducts of tin(IV) chloride with urea, thiourea and alkyl substituted urea and thiourea, have been synthesized with the purpose of obtaining the enthalpies involved in the formation of the adducts. The effect of the substitution of hydrogen atoms in urea or thiourea by alkyl groups, over the energy of the Sn–O or Sn–S bonds, is also studied.

Correlations between the bond energies and the basicity of the ligands, are also established.

## 2. Experimental

Due to the moisture sensitivity of the compounds, all preparations and manipulations were made under a dry nitrogen atmosphere.

### 2.1. Chemicals

Tin(IV) chloride (99%, Aldrich Chemical Company) was purified by the method of Hildebrand and Caster [6]. Tetramethylurea (99%, Fluka AG Buchs SG) was purified by distillation through an efficient column (bp 113–114°C). Urea (99%, Aldrich Chemical Company), 1,1-dimethylurea (99%, Aldrich

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Chemical Company) 1,3-dimethylurea (99% Aldrich Chemical Company), thiourea (PA, Aldrich Chemical Company), tetramethylthiourea (RP, Fluka AG Buchs SG) and 1-allyl-2-thiourea (98%, Aldrich Chemical Company) were purified by recrystallization from chloroform or methanol (mp = 134–135, 177–178, 100–101, 171–172, 74–75 and 69–70°C, respectively). Solvents used in the synthesis of the adducts and calorimetric measurements were purified by distillation and stored over Linde 4 Å molecular sieves.

## 2.2. Analytical

Carbon, hydrogen and nitrogen contents were determined by microanalytical procedures. Tin was determined by gravimetry, following hydrolysis of the adducts samples in boiling aqueous 2% ammonium nitrate solution. The precipitate was filtered, washed free of chloride with 2% ammonium nitrate solution, ignited and weighted as SnO<sub>2</sub>. Chloride content of the sample was determined in the filtrate by gravimetry using N/10 AgNO<sub>3</sub> solution.

## 2.3. Synthesis of the complexes

The adducts were synthesized by the reaction of tin(IV) chloride and ligands in solution. A typical procedure is given below.

### 2.3.1. SnCl<sub>4</sub>-1,3-dmu

On mixing a solution of SnCl<sub>4</sub> in 10 ml of chloroform, under a dry nitrogen current, a viscous layer appeared. The stirring during several hours changed the layer into a white solid. This was filtered, washed with several portions of petroleum ether and dried for several hours in vacuum. The compound was recrystallized from nitromethane, dried in vacuum and stored in a desiccator over calcium chloride. Most of the adducts were obtained from methanol solutions. Some adducts did not form as viscous layers. Other form as viscous layers that did not change into solids. It was necessary scratching these layers, after decantation, with a mixture of *n*-hexane–*n*-pentane and freezing for several hours.

## 2.4. IR spectra

Spectra were obtained with samples in KBr matrix for adducts and solid ligands. For liquid

ligands, a film of the ligand sandwiched between NaCl plates was used. A Perkin–Elmer 1600 series FTIR spectrophotometer in the 4000–400 cm<sup>-1</sup> region was used.

## 2.5. Thermal studies

TG and DSC measurements were obtained in an argon atmosphere in a Du Pont 951 TG analyser with samples varying in mass from 6.63 to 11.07 mg (TG-DTG) and from 1.72 to 2.14 mg (DSC) and a heating rate of 10 K min<sup>-1</sup> in the 298–673 K (DSC) and 298–1173 K (TG-DTG) temperature ranges. TG calibration for temperature was made using metallic aluminium as a standard (mp = 660.37°C) and the calibration for weight was carried out by using calcium oxalate as a standard. The DSC calibration was made using metallic indium as a standard (mp = 165.73°C,  $\Delta_s H^\theta = 28.4 \text{ J g}^{-1}$ ).

## 2.6. Calorimetric measurements

All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described elsewhere [7]. The solution calorimetric measurements were performed by dissolving samples of 10.7–285.9 mg of the adducts or tin(IV) chloride in 100 ml of methanol, and the ligand in this last solution maintaining a molar relation equal to the stoichiometry of the adduct. The accuracy of the calorimeter was carried out by determining the heat of dissolution of tris[(hydroxymethyl)amino]methane in 0.1 mol dm<sup>-3</sup> HCl. The result ( $-29.78 \pm 0.03 \text{ kJ mol}^{-1}$ ) is in agreement with the value recommended by IUPAC [8] ( $-29.763 \pm 0.003 \text{ kJ mol}^{-1}$ ).

## 3. Results and discussion

All the adducts obtained were solids. The yields range from 36 to 93%. The yields, melting points, colors, appearance and analytical data are summarized in Table 1.

### 3.1. Infrared data

The more important IR bands are reported in Table 2. A strong band is observed in the region

Table 1  
Yields in % on preparation, melting points, appearance and analytical data of the compounds

Compound	Yield	MP <sup>a</sup> (°C)	Appearance <sup>b</sup>	C		H		N		Cl		Sn	
				Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found	Calcd.	Found
[SnCl <sub>4</sub> (u) <sub>2</sub> ]	58	348–350	wh. cr.	6.31	6.27	2.12	2.18	14.72	14.55	37.26	37.07	31.18	31.02
[SnCl <sub>4</sub> (1,1-dmu) <sub>2</sub> ]	73	174–175	wh. pw.	16.50	16.24	3.69	3.78	12.83	12.77	32.47	32.35	27.18	27.08
[SnCl <sub>4</sub> (1,3-dmu) <sub>2</sub> ]	80	220–221	wh. pw.	16.50	16.28	3.69	3.71	12.83	12.67	32.47	32.37	27.18	27.05
[SnCl <sub>4</sub> (tmu) <sub>2</sub> ]	65	194–195	wh. cr.	24.37	24.07	4.91	4.93	11.37	11.07	28.78	28.87	24.08	24.52
[SnCl <sub>4</sub> (tu) <sub>2</sub> ]	69	152–153	wh. pw.	5.82	5.75	1.95	2.03	13.57	13.33	34.36	34.16	28.76	28.66
[SnCl <sub>4</sub> (tmtu) <sub>2</sub> ]	36	200–201	wh. pw.	22.88	22.75	4.61	4.61	10.67	10.56	27.01	26.99	22.61	22.59
[SnCl <sub>4</sub> (atu) <sub>2</sub> ]	93	204–205	wh. pw.	19.50	19.37	3.27	3.29	11.37	11.16	28.77	28.59	24.08	24.02

<sup>a</sup> With decomposition.

<sup>b</sup> wh., white; cr., crystals; pw., powder.

1628–1579 cm<sup>-1</sup> for the amide adducts. This band is assigned to the C=O stretching vibration ( $\nu_{C=O}$ ). Considerable shifts to lower frequencies of  $\nu_{C=O}$  in the adducts respect to the free ligands are observed. This is indicative of coordination of the oxygen atom of the ligands to the tin(IV) chloride [1,9]. In some cases it is also observed positive shifts of the C–N stretching frequency ( $\nu_{C-N}$ ) [1,9]. Positive shifts of the N–H stretching frequencies ( $\nu_{N-H}$ ) after coordination were also observed [10].

For thioamides adducts, a strong band is observed in the region 1124–1105 cm<sup>-1</sup>. This is attributed to C=S stretching frequency [11]. It is observed negative shifts of this frequency after coordination in the

adducts relative to free ligands, indicating coordination of the ligands through the sulphur atom to the tin(IV) chloride [11].

### 3.2. Thermal studies

Thermogravimetry and derivative thermogravimetry of the adducts show that the thermal dissociation processes of the adducts were of different types:

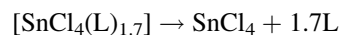
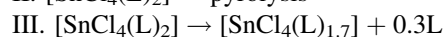
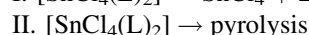
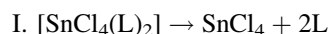


Table 2  
Main IR absorption bands (cm<sup>-1</sup>) of complexes and free ligands

Compound	Assignment <sup>a</sup>					
	$\nu_{NH}$	$\delta_{NH}$	$\nu_{CO}/\nu_{CS}$	$\nu_{CN}$	$R_{NH}$	
u	3461s, 3350s	1622s	1670s	1458s		n.o.
[SnCl <sub>4</sub> (2u) <sub>2</sub> ]	3480s, 3360s	1544s	1621s	1505s		n.o.
1,1-dmu	3403s, 3198s	1607s	1666s	1401s		1275s, 1103s
[SnCl <sub>4</sub> (1,1-dmu) <sub>2</sub> ]	3455s, 3359s	1601s	1628s	1428s		1278m, 1094m
1,3-dmu	3373s	1578s	1638s	1413m		1287m, 1175m
[SnCl <sub>4</sub> (1,3-dmu) <sub>2</sub> ]	3394s	1593s	1622s	1448m		1185m
tmu			1644s	1504s, 1377s		
[SnCl <sub>4</sub> (tmu) <sub>2</sub> ]		1612s	1579s	1520s, 1414s		
tu	3381s	1619vs	1156m	1474s		n.o.
[SnCl <sub>4</sub> (tu) <sub>2</sub> ]	3440s	1616vs	1105m	1424s		n.o.
tmtu			1117s	1361vs		
[SnCl <sub>4</sub> (tmtu) <sub>2</sub> ]			1114s	1386vs		
atu	3440s	1628vs	1133s	1435s		n.o.
[SnCl <sub>4</sub> (atu) <sub>2</sub> ]	3500sh	1594vs	1124m	1465s		n.o.

<sup>a</sup>  $\nu$ , stretching;  $\delta$ , angular deformation;  $R$ , rocking. Intensity of bands: vs, very strong; s, strong; m, medium; sh, shoulder; n.o., not observed.

Table 3  
Thermoanalytical data of the compounds

Compound	% mass lost		TG temperature range (K)	Species lost	DSC peak temperature (K)	$\Delta H^\theta$ (kJ mol <sup>-1</sup> )
	Calcd.	Obs.				
[SnCl <sub>4</sub> (u) <sub>2</sub> ]	100	97.8 2.2 <sup>b</sup>	499 – 565	-[SnCl <sub>4</sub> (u) <sub>2</sub> ] <sup>a</sup>	448	-128.61
[SnCl <sub>4</sub> (1,1-dmu) <sub>2</sub> ]	6.1	6.2	332 – 365	-0.3 dmu	452	71.49
	94.0	89.9 1.8 <sup>b</sup>	365 – 551	-1.7dmu -SnCl <sub>4</sub>	499	-629.75
[SnCl <sub>4</sub> (1,3-dmu) <sub>2</sub> ]		99.0	498 – 531	-[SnCl <sub>4</sub> (dmu) <sub>2</sub> ] <sup>a</sup>	349 499 <sup>c</sup>	34.18 -547.65
[SnCl <sub>4</sub> (tmu) <sub>2</sub> ]	100	99.5	441 – 485	-[SnCl <sub>4</sub> (tmu) <sub>2</sub> ] <sup>a</sup>	463 481	-51.66 -259.91
[SnCl <sub>4</sub> (tu) <sub>2</sub> ]	100	49.1	493 – 583	pyrolysis	352	5.01
		14.5	583 – 948		407	57.54
		35.0 <sup>b</sup>			478	-66.62
[SnCl <sub>4</sub> (tmtu) <sub>2</sub> ]	100	98.1 1.9 <sup>b</sup>	483 – 537	-[SnCl <sub>4</sub> (tmtu) <sub>2</sub> ] <sup>a</sup>	545	-61.25
[SnCl <sub>4</sub> (atu) <sub>2</sub> ]	100	67.6	500 – 655	pyrolysis	496 <sup>d</sup>	-265.81
		7.9	980 – 1073			
		24.5 <sup>b</sup>				

<sup>a</sup> Pyrolysis.

<sup>b</sup> Residue at 1173 K.

<sup>c</sup> Two overlapping peaks.

<sup>d</sup> Three overlapping peaks.

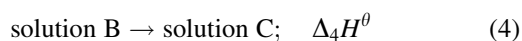
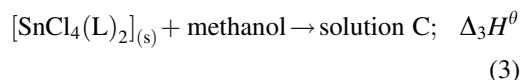
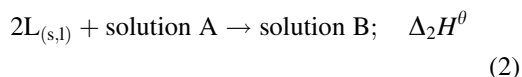
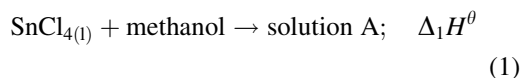
The adducts of urea, 1,3-dimethylurea, tetramethylurea and tetramethylthiourea followed process I, eliminating SnCl<sub>4</sub> and ligand together in one step. The adducts of thiourea and allylthiourea followed process II, with pyrolysis of the adduct leaving a residue that is probably tin in the case of atu and a mixture of carbon and tin in the case of tu. The adduct of 1,1-dimethylurea followed the process III, with elimination of part of the ligand in a first step, followed by the elimination of the rest of the ligand and SnCl<sub>4</sub> together in a second step.

The DSC curves of the adducts are consistent with the TG-DTG data. They showed endothermic peaks due to the partial elimination of ligand and exothermic peaks due to the pyrolysis of the adduct or the intermediate product formed. Table 3 lists the thermoanalytical data of the adducts.

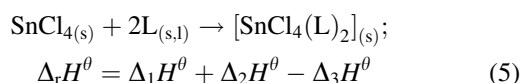
### 3.3. Calorimetric measurements

The standard enthalpies of dissolution of tin(IV) chloride, ligands and adducts were obtained as previously reported [12]. The standard enthalpies of

dissolution were obtained according to the standard enthalpies of reactions (1)–(4) in solution:



The application of Hess's law to the series of reactions (1)–(4) gives the standard enthalpies of the acid/base reactions ( $\Delta_r H^\theta$ ), according to the reaction (5)



since the final state of reactions (2) and (3), is the same and  $\Delta_4 H^\theta = 0$ .

Table 4 gives the values obtained for the enthalpies of dissolution of tin(IV) chloride ( $\Delta_1 H^\theta$ ), ligand into

Table 4  
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	Number of experiments	$\Delta_r H^\theta$ (kJ mol <sup>-1</sup> ) <sup>a</sup>
SnCl <sub>4</sub>	methanol	34	( <i>i</i> = 1) -129.73 ± 1.20
u(s)	2 : 1 SnCl <sub>4</sub> -methanol	5	( <i>i</i> = 2) 13.40 ± 0.88
[SnCl <sub>4</sub> (u) <sub>2</sub> ](s)	methanol	4	( <i>i</i> = 3) -6.08 ± 0.24
1,1-dmu(s)	2 : 1 SnCl <sub>4</sub> -methanol	5	( <i>i</i> = 2) 2.92 ± 0.51
[SnCl <sub>4</sub> (1,1-dmu) <sub>2</sub> ](s)	methanol	4	( <i>i</i> = 3) 6.36 ± 0.33
1,3-dmu(s)	2 : 1 SnCl <sub>4</sub> -methanol	5	( <i>i</i> = 2) 19.87 ± 0.57
[SnCl <sub>4</sub> (1,3-dmu) <sub>2</sub> ](s)	methanol	4	( <i>i</i> = 3) 3.41 ± 0.13
tmu(l)	2 : 1 SnCl <sub>4</sub> -methanol	5	( <i>i</i> = 2) -7.46 ± 0.06
[SnCl <sub>4</sub> (tmu) <sub>2</sub> ](s)	methanol	5	( <i>i</i> = 3) 32.08 ± 0.75
tu(s)	2 : 1 SnCl <sub>4</sub> -methanol	6	( <i>i</i> = 2) 19.93 ± 0.37
[SnCl <sub>4</sub> (tu) <sub>2</sub> ](s)	methanol	4	( <i>i</i> = 3) 50.43 ± 1.05
tmtu(s)	2 : 1 SnCl <sub>4</sub> -methanol	5	( <i>i</i> = 2) 53.07 ± 1.34
[SnCl <sub>4</sub> (tmtu) <sub>2</sub> ](s)	methanol	5	( <i>i</i> = 3) 58.38 ± 1.52
atu(s)	2 : 1 SnCl <sub>4</sub> -methanol	6	( <i>i</i> = 2) 46.09 ± 0.56
[SnCl <sub>4</sub> (atu) <sub>2</sub> ](s)	methanol	4	( <i>i</i> = 3) -13.13 ± 0.70

<sup>a</sup> The deviations of the enthalpies values were calculated up to the second decimal figure to maintain the uniformity and indicating the number of significant figures used in the measurements. Really, they should be approached to suitable values.

the solution of SnCl<sub>4</sub> ( $\Delta_2 H^\theta$ ) and of the adducts ( $\Delta_3 H^\theta$ ). Uncertainty intervals given in this table are twice the standard deviations of the means of about five replicate measurements on each compound. Combined errors were calculated from the square root of the sum of the square of the component errors.

From the values obtained for the standard enthalpies of the acid/base reactions ( $\Delta_r H^\theta$ ) and using appropriate thermochemical cycles [7,13], the following thermochemical parameters were determined: the standard enthalpies of formation ( $\Delta_f H^\theta$ ), the standard enthalpies of decomposition ( $\Delta_D H^\theta$ ), the standard lattice enthalpies ( $\Delta_M H^\theta$ ) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ( $\Delta_r H^\theta(g)$ ). These last values can be used to calculate the standard enthalpies of the Sn–O and Sn–S bonds [13], being equal to  $\bar{D}(\text{Sn–O})$  or  $\bar{D}(\text{Sn–S}) = -\Delta_r H^\theta(g)/2$ . Table 5 lists the values obtained for all these thermochemical parameters. For the determination of  $\Delta_r H^\theta(g)$  it was necessary to assume that the molar standard enthalpies of sublimation of the adducts were equal to the enthalpies of sublimation or vaporization of 1 mol of the respective ligand [24,25], as melting points and thermal studies showed that the adducts decomposed on heating and were not found in the liquid phase and probably, not in the gaseous phase. For the calculation of the thermochemical parameters of the adduct of allyl-thiourea, it was

necessary to calculate the standard enthalpies of formation and sublimation of the ligand as their values are not found in the literature. They were calculated by a group contribution method [26–28], from the enthalpies values for thiourea.

Based on the  $\Delta_r H^\theta$  values for the adducts, we obtain the basicity order: tmu > tu > tmtu > 1,3-dmu > u > 1,1-dmu > atu. The same sequence is obtained by using the values of  $\bar{D}(\text{Sn–O})$  and  $\bar{D}(\text{Sn–S})$  except by the inversion between tmu and tu. The expected order on the basis of an inductive effect would be that in which the amides are better bases than the thioamides due to the electronegativity value of the oxygen atom. Among the amides or thioamides, those with greater substitution of hydrogen atoms by methyl groups would be the better bases, due to the electron-donating character of the methyl groups. Those with substitution of a hydrogen atom by the electron withdrawing allyl group, would be the worst bases. Thus, tmu > 1,3-dmu  $\cong$  1,1-dmu > u and tmtu > tu > atu. The first expected sequence is observed with the exception of 1,1-dmu that is the worst base. Probably a steric hindrance would be in action and/or because the group N(CH<sub>3</sub>)<sub>2</sub> is less electronegative than the group NH<sub>2</sub>, canceling the inductive effect created by the two methyl groups, leading 1,1-dmu to be the worst base. The second sequence is also observed with the exception of tu that is the best base.

Table 5  
Summary of the thermochemical results (kJ mol<sup>-1</sup>)

Compound	$\Delta_r H^\theta$	$\Delta_f H^\theta$	$\Delta_s^\ddagger H^\theta$ or $\Delta_l^\ddagger H^\theta$	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta(\text{g})$	$\bar{D}(\text{Sn-O})$ or $\bar{D}(\text{Sn-S})$
SnCl <sub>4</sub>		-511.3 <sup>a</sup>	39.8 <sup>a</sup>				
u <sub>(S)</sub>		-333.7 ± 0.1 <sup>b</sup>	87.8 ± 2.1 <sup>b</sup>				
1,1-dmu <sub>(S)</sub>		-319.06 ± 0.68 <sup>c</sup>	89.1 ± 1.9 <sup>d</sup>				
1,3-dmu <sub>(S)</sub>		-295 ± 17 <sup>e</sup>	85.4 <sup>e</sup>				
tmu <sub>(l)</sub>		-60.8 <sup>f</sup>	51.12 ± 0.73 <sup>g</sup>				
tu <sub>(S)</sub>		-89.12 ± 0.12 <sup>h</sup>	93.7 ± 4.7 <sup>i</sup>				
tmtu <sub>(S)</sub>		-38.3 ± 2.3 <sup>j</sup>	83.03 ± 0.20 <sup>j</sup>				
atu <sub>(S)</sub>		-13.0 ± 2.6 <sup>k</sup>	118.7 ± 1.5 <sup>k</sup>				
[SnCl <sub>4</sub> (u) <sub>2</sub> ] <sub>(S)</sub>	-110.25 ± 1.49	-128.90 ± 1.8		-325.7 ± 4.9	285.9 ± 4.5	-237.9 ± 5.3	119.0 ± 2.7
[SnCl <sub>4</sub> (1,1-dmu) <sub>2</sub> ] <sub>(S)</sub>	-103.17 ± 1.34	-1252.6 ± 2.2		-321.2 ± 4.5	281.4 ± 4.0	-232.1 ± 4.9	116.1 ± 2.5
[SnCl <sub>4</sub> (1,3-dmu) <sub>2</sub> ] <sub>(S)</sub>	-113.27 ± 1.33	-1215 ± 17		-323.9 ± 2.6	284.1 ± 2.4	-238.5 ± 3.3	119.3 ± 1.7
[SnCl <sub>4</sub> (tmu) <sub>2</sub> ] <sub>(S)</sub>	-169.27 ± 1.42	-602.2 ± 4.4		-231.7 ± 2.9	271.51 ± 2.04	-260.2 ± 3.0	130.1 ± 1.5
[SnCl <sub>4</sub> (tu) <sub>2</sub> ] <sub>(S)</sub>	-160.23 ± 1.64	-849.8 ± 2.2		-387.4 ± 9.7	347.6 ± 9.5	-293.7 ± 4.2	156.0 ± 2.1
[SnCl <sub>4</sub> (tmtu) <sub>2</sub> ] <sub>(S)</sub>	-135.04 ± 2.35	-722.9 ± 5.3		-340.9 ± 3.1	301.10 ± 2.38	-257.9 ± 3.1	128.9 ± 1.6
[SnCl <sub>4</sub> (atu) <sub>2</sub> ] <sub>(S)</sub>	-70.5 ± 1.50	-607.8 ± 2.4		-347.7 ± 3.9	307.9 ± 3.4	-229.0 ± 4.2	114.5 ± 2.1

<sup>a</sup> [14].

<sup>b</sup> [15].

<sup>c</sup> [16].

<sup>d</sup> [17].

<sup>e</sup> [18].

<sup>f</sup> [19].

<sup>g</sup> [20].

<sup>h</sup> [21].

<sup>i</sup> [22].

<sup>j</sup> [23].

<sup>k</sup> See text.

Probably a steric hindrance due to the four methyl groups is in action in tmu and/or because the inductive effect of increasing the electronic density on the sulphur atom caused by the four methyl groups, also cause too much softness of the sulphur atom, leading tmtu to be a worst base than tu. According to hard/soft acid/base (HSAB) [29–31], we expect the amides to be hard, the thioamides to be soft and Sn(IV) to be soft. Then, the thioamides are the best bases for Sn(IV). It is also observed with the exceptions of tmu that is the best base and atu that is the worst. Substitution of hydrogen atoms by methyl groups leads to a relative softness of the amide. This could explain the position of tmu. With respect to atu, substitution of a hydrogen atom by the allyl group leads to a relative hardness of the thioamide. This could explain the position of atu as the worst base for SnCl<sub>4</sub>. Also it could be suffering a steric hindrance due to the longness of the allyl group and the decreasing of the electronic density on the

sulphur atom by an inductive effect of the electron withdrawing allyl group.

As a whole we observed that the mean tin-oxygen coordinate bond dissociation energies of the amide complexes of tin(IV) chloride are weaker than the tin-sulphur bond energies in comparable to thioamide complexes.

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