Thermochemistry of adducts of tin(IV) chloride with ligands containing amide or thioamide groups

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Abstract

The compounds $[SnCl_4(L)_2]$ (where L is formamide (fa), acetamide (a), *N,N*-dimethylformamide (dmf), *N,N*-dimethylaceta-mide (dma), benzamide (ba), thioacetamide (ta), *N,N*-dimethylthioformamide (dmtf), *N,N*-dimethylthioacetamide (dmta) or thiobenzamide (tba), were synthesized and characterized by melting point, 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 ($\Delta_r H^\theta(g)$). The mean standard enthalpies of the tin(IV)–oxygen ($\overline{D}_{(Sn-O)}$) and tin(IV)–sulphur bonds ($\overline{D}_{(Sn-O)}$) have been estimated. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

In a recent article [1] we described the preparation, characterization and thermochemistry of adducts of tin(IV) chloride with substituted urea and thiourea. In this article we describe the synthesis of adducts of tin(IV) chloride with substituted acetamide and thioa-cetamide to obtain the enthalpies of formation of the adducts. The effect of substitution of hydrogen atoms in acetamide or thioacetamide by methyl groups and the substitution of a methyl group by a phenyl group or by a hydrogen atom, on the energy of the Sn–O or Sn–S bonds, is also studied. Correlations between the bond energies and the basicity of the ligands and with

the bond energy values obtained for the adducts of urea and thioures derivatives [1], 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 Inc.) was purified by the method of Hildebrand and Caster [2]. Formamide (99%, Carlo Erba), dimethyl-formamide (99%, Riedel-deHaem), dimethylaceta-mide (99% z.s., Merck) and dimetylthioformamide (99% Aldrich Chemical Company Inc.) were purified

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by distillation through an efficient column (bp = 207, 150, 162 and 55°C/3 mmHg, respectively). Acetamide (99% Carlo Erba), benzamide (98% z.s., Merck), thioacetamide (99% p.a., Merck), dimethylthioacetamide (Eastman) and thiobenzamide (Aldrich Chemical Company Inc.) were purified by recrystallation from suitable solvents (mp = 78–80, 123–124, 109–110 and 70–71°C, respectively). Solvents used in the synthesis of the adducts 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 content was determined by gravimetry as stannic oxide, following precipitation of hydrated stannic oxide by ammonia solution from the nitric acid solutions of the adducts. The precipitate was ignited to stannic oxide. The filtrate was used for the gravimertic determination of the chloride content as silver chloride, using 0.1 M AgNO$_3$ solution. Samples were amide or thioamide interfered with the estimation of tin as given above, were reacted with concentrated HNO$_3$ and the method was finished as before. Chloride content in these latter samples was determined gravimetrically as silver chloride after refluxing for several hours with sodium carbonate solution.

2.3. Synthesis of the adducts

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

2.3.1. SnCl$_4$–dma
On mixing a solution of 0.50 ml (4.27 mmol) of SnCl$_4$ in 10 ml of petroleum ether with 0.40 ml (8.60 mmol) of dma, under a dry nitrogen current, a white solid appeared. The stirring was kept during several hours. The solid was filtered, washed with three portions of 10 ml of petroleum ether and dried for several hours in vacuum. The compound was recrystallized from diclorethane, dried in vacuum and stored in a desiccator over calcium chloride. Most of the adducts were obtained from chloroform solutions. All the adducts were prepared with a molar ratio tin(IV)/ligand of 1/2. The most of them were washed

with petroleum ether. The acetamide adduct is obtained as a viscous layer that changed into a solid after drying for several hours in vacuum.

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^{-1} region was used.

2.5. Thermal studies

TG/DTG and DSC measurements were obtained in an argon atmosphere using a Du Pont 951 TG analyzer with samples varying in mass from 7.73 to 11.75 mg (TG/DTG) and from 3.77 to 7.41 mg (DSC) and a heating rate of 10 K min^{-1} in the 298–673 (DSC) and 298–1173 K (TG/DTG) temperature ranges. TG calibration for temperature was made using metallic aluminum as a standard (mp = 660.37°C) and the calibration for mass was carried out automatically. The DSC calibration was made using metallic indium as a standard (mp = 165.73°C, $\Delta_s^l H^\theta = 28.4$ 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 [3]. The solution calorimetric measurements were performed by dissolving samples from 2.2 to 256 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^{-3} HCl. The result (−29.78± 0.03 kJ mol^{-1}) is in agreement with the value recommended by IUPAC [4] (−29.763 ± 0.000 kJ mol^{-1}).

3. Results and discussion

All the adducts obtained were solids. The yields ranged from 45 to 99%. The yields, melting points, colors, appearance and analytical data are summarized

Table 1
Yields, melting points, appearance and analytical data of the adducts

Compound	Yield (%)	Melting point[a] (°C)	Appearance	C		H		N		Sn		Cl	
				Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
[SnCl₄(fa)₂]	73	75	White powder	–	–	–	–	7.99	8.20	33.85	33.44	40.45	40.28
[SnCl₄(a)₂]	99	98–9	White powder	12.69	12.43	2.66	2.66	7.40	7.18	31.35	31.43	37.45	37.32
[SnCl₄(dmf)₂]	86	184–5	White powder	–	–	–	–	6.89	6.72	29.18	28.98	34.87	34.68
[SnCl₄(dma)₂]	54	145	White powder	22.10	21.92	4.17	4.14	6.44	6.27	27.30	27.09	32.62	32.34
[SnCl₄(ba)₂]	82	220	Light yellow powder	33.45	33.34	2.81	2.79	5.57	5.40	23.61	23.61	28.21	28.39
[SnCl₄(ta)₂]	83	160	Light yellow powder	11.70	11.53	2.45	2.48	6.82	6.60	28.89	29.04	34.52	34.64
[SnCl₄(dmtf)₂]	45	180	Light yellow powder	–	–	–	–	6.38	6.49	27.05	26.94	32.32	32.18
[SnCl₄(dmta)₂]	85	152	White powder	20.58	20.36	3.89	3.85	6.00	5.78	25.42	25.58	30.37	30.15
[SnCl₄(tba)₂]	90	320	Yellow powder	31.44	31.22	2.64	2.63	5.24	5.16	22.19	22.24	26.51	26.30

[a] Melting point most with decomposition.

in Table 1. For the adducts of fa, dmf and dmtf, it is not obtained a good C/H analysis indicating a interference of metallic tin with the determination of these contents.

3.1. Infrared data

The more important IR bands are reported in Table 2. If coordination occurs through nitrogen, the double bond character of the amide or thioamide group C=O or C=S increase and that of C=N decrease, resulting in a increase of the CO or CS stretching frequency and a decrease of the CN stretching frequency. Coordination through oxygen contrary leads to the decrease of the double bond character of C=O or C=S and the increase in the double bond character of C=N, resulting in a decrease of the CO stretching frequency and an increase of the CN stretching frequency [5,6]. Also, the NH stretching frequency will decrease on the formation of the adduct using the nitrogen atom and no appreciable change will be

Table 2
Main IR absorption bands (cm^{-1}) of adducts and free ligands

Compound	Assignment[a]			
	ν_{NH}	Amide I (ν_{CO}/ν_{CS})	Phenyl	Amide II ($\nu_{CN} + \delta_{NH}$)
fa	3325vs	1685vs		n.o.
[SnCl₄(fa)₂]	3351s	1683vs		1569s
a	3191s	1666vs		n.o.
[SnCl₄(a)₂]	3365s	1653vs		1560m
dmf		1673s		
[SnCl₄(dmf)₂]		1629s		
dma		1645vs		
[SnCl₄(dma)₂}		1603vs		
ba	3171s	1660vs	1580vs	n.o.
[SnCl₄(ba)₂]	3264m	1640vs	1596s	1534s
ta	3303s	720s		
[SnCl₄(ta)₂]	3330s	694s		
dmtf		969s		
[SnCl₄(dmtf)₂]		911s		
dmta		864m, 655m		
[SnCl₄(dmta)₂]		844m, 648m		
tba	3360s	687s	1598m	1520sh
[SnCl₄(tba)₂]	3340m	683s		1525sh

[a] ν, Stretching; δ, angular deformation. Intensity of bands: vs, very strong; s, strong; m, medium; sh, shoulder; n.o., not observed.

observed when the adduct is formed using the oxygen atom [5,6]. The IR spectra of the amide or thiamide adducts showed negative shifts of the carbonyl or thiocarbonyl stretching frequencies and positive shifts in the CN stretching frequencies, both with respect to free ligands, suggesting coordination through the oxygen or sulphur atom. Positive shifts of NH stretching frequencies were also observed [7].

3.2. Thermal studies

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

I : $[SnCl_4(L)_2] \rightarrow SnCl_4 + 2L$

II : $[SnCl_4(L)_2] \rightarrow pyrolisis$

III : $[SnCl_4(L)_2] \rightarrow [SnCl_4(L)_x] + (2-x)L, \quad [SnCl_4(L)_x] \rightarrow pyrolisis$

IV : $[SnCl_4(L)_2] \rightarrow ySnCl_4 + [(SnCl_4)_{(1-y)}(L)_2], \quad [(SnCl_4)_{(1-y)}(L)_2] \rightarrow pyrolisis$
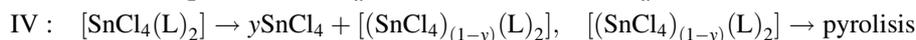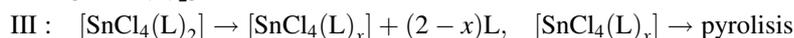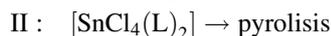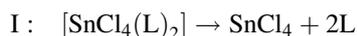
The adduct of fa followed process I eliminating $SnCl_4$ and ligand in one step. The adducts of a, dmf, dma and ba followed process II with pyrolysis of the adduct leaving a residue that is probably tin or a mixture of tin and carbon [8]. The adducts of dmtf and dmta followed process III with elimination of part of the ligand in a first step, followed by the pyrolysis of the intermediate product in a second step leaving a residue. The adducts of ta and tba followed process IV with elimination of part of $SnCl_4$ in a first step followed by the pyrolysis of the intermediate product in a second step, leaving also a residue. The DSC curves of the adducts are consistent with the TG-DTG data. They showed endothermic peaks due to partial elimination of ligand, melting, partial elimination of ligand with melting, partial eliation of $SnCl_4$ or partial eliation of SnCl and ligand. Exothermic peaks are also observed, due to pyrolysis of intermediate products or ligands. 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 [8]. The standard enthalpies of dissolution were obtained according to the standard enthalpies of reactions (1)–(4) in solution

$$SnCl_{4(l)} + methanol \rightarrow solution\,A; \quad \Delta_1 H^\theta \qquad (1)$$

$$2L_{(s,l)} + solution\,A \rightarrow solution\,B; \quad \Delta_2 H^\theta \qquad (2)$$

$$[SnCl_4(L)_2]_{(s)} + methanol \rightarrow solution\,C; \quad \Delta_3 H^\theta \qquad (3)$$

$$solution\,B \rightarrow solution\,C; \quad \Delta_4 H^\theta \qquad (4)$$
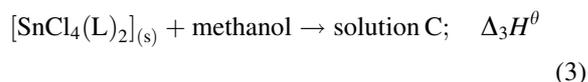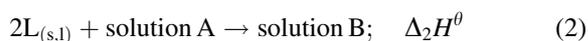
The application of Hess' law to the series of reactions (1)–(4) gives the standard enthalpies of the acid/base reactions ($\Delta_r H^o$) according to the reaction (5)

$$SnCl_{4(l)} + 2L_{(s,l)} \rightarrow [SnCl_4(L)_2]_{(s)};$$
$$\Delta_r H^\theta = \Delta_1 H^\theta + \Delta_2 H^\theta - \Delta_3 H^\theta \qquad (5)$$
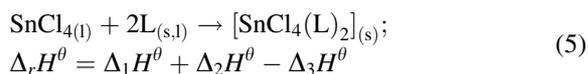
since the final state of reactions (2) and (3) is the same and $\Delta_4 H^\theta = 0$.

Table 4 gives the values obtained for the enthalpies of dissolution of tin(IV) chloride ($\Delta_1 H^\theta$), ligands into the solution of $SnCl_4$ ($\Delta_2 H^\theta$) and of the adducts ($\Delta_3 H^\theta$). Uncertainty intervals given in this table are twice the standard deviations of the mean of 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 [3,6], the following thermochemical parameters were determined: the standard enthalpies of formation ($\Delta_f H^\theta$), the standard enthalpies of decomposition ($\Delta_D H$), 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 [6], being equal to $\overline{D}_{(Sn-O)}$ or $\overline{D}_{(Sn-S)} = -\Delta_r H^\theta(g)/2$. 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 mole of the respective ligand [15,16], as melting

Table 3
Thermoanalytical data of the adducts

Compound	Mass lost (%)		TG temperature range (K)	Species lost	DSC peak temperature (K)	$\Delta_i H^\theta$ (kJ mol^{-1})
	Calculated	Observed				
[SnCl$_4$(fa)$_2$]	100	100	469–549	SnCl$_4$–2fa[a]	349	19.6
					501	−218.3
[SnCl$_4$(a)$_2$]	100	95.5	487 – 555	[SnCl$_4$(a)$_2$][a]	450	13.6
		4.8[b]			500	−409.7
[SnCl$_4$(dmf)$_2$]	100	98.8	483 – 525	[SnCl$_4$(dmf)$_2$][a]	421	11.3
		2.0[b]			484	121.0
[SnCl$_4$(dma)$_2$]	100	97.1	474–562	[SnCl$_4$(dma)$_2$][a]	427	9.2
		2.9[b]			500	−392.1
[SnCl$_4$(ba)$_2$]	100	99.0	502–540	[SnCl$_4$(ba)$_2$][a]	472	−116.6
		1.6[b]			509	−123.1
[SnCl$_4$(ta)$_2$]	65.9	64.0	436–502	0.75SnCl$_4$–ta[a]	427	21.0
	4.6	4.5	809–844	0.25ta	447	−103.9
	12.8	12.3	973 – 1089	0.70ta		
		20.0[a]				
[SnCl$_4$(dmtf)$_2$]	10.2	11.5	349–394	0.5dmtf	461	−22.9
	83.8	84.9	394 – 551	SnCl$_4$–1.2dmtf[a]	513	−83.3
		4.0[b]				
[SnCl$_4$(dmta)$_2$]	4.4	4.5	338 – 366	0.2dmta	371	11.3
	80.1	80.1	366–530	SnCl$_4$–1.1dmta		
		12.1[b]				
[SnCl$_4$(tba)$_2$]	69.9	69.4	472–515	SnCl$_4$–1.3tba	480	165.4
	3.9	3.1	840–886	0.15tba	495	−410.1
	5.1	5.6	1001–1072	0.20tba		
		25.6[b]				

[a] Pyrolysis.
[b] Residue at 1173 K.

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 adducts of ba, fa and tba, it was necessary to calculate the standard enthalpies of formation and sublimation or vaporization of the ligands as their values are not found in the literature. They were calculated by a group contribution method [14,17,18], from the enthalpy values for acetamide, dimethylformamide and benzamide, respectively.

Based on the $\Delta_r H^\theta$ values for the adducts, we obtain the basicity order: dma > dmf > dmtf > fa > tba > ta > ba > a. Using the values of $\overline{D}_{(Sn-O)}$ and $\overline{D}_{(Sn-O)}$ we obtain: tba > dma > dmf = dmtf > ba > ta > fa > a. 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 be bigger than that of the

sulphur atom. Among the amides or thioamides, those with the greater substitution of hydrogen atoms by methyl groups would be the best bases, due to the electron-donating character of the methyl group. The contrary is true for the electron-withdrawing phenyl group. Thus, dma > dmf > a > fa > ba and dmf > dmtf > ta > tba. The first sequence is observed with the exception of the inverton among the three last members. The second sequence is also observed with the inverton between ta and tba. Formamide and thiobenzamide could be better bases than expected if other kind of interaction is present, as hydrogen bonds in the case of fa and the participation of the phenyl ring in the bond Sn–S in the case of tba.

According to hard/soft acid/base (HSAB) [19–21], we expect the amides to be hard, the thioamides to be soft and tin(IV) chloride to be soft. Then, the thioamides are the best bases for SnCl$_4$. It is observed: tba > ba and ta > a but dmf > dmtf. Substitution of

Table 4
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	Number of experiments	$\Delta_i H^\theta$ (kJ mol^{-1})
SnCl$_{4(l)}$	Methanol	41 ($i = 1$)	-128.99 ± 0.61
fa$_{(l)}$	2:1 SnCl$_4$–methanol	3 ($i = 2$)	4.94 ± 0.27
[SnCl$_4$(fa)$_2$]$_{(s)}$	Methanol	5 ($i = 3$)	20.65 ± 0.69
a$_{(s)}$	2:1 SnCl$_4$–methanol	5 ($i = 2$)	25.11 ± 0.61
[SnCl$_4$(a)$_2$]$_{(s)}$	Methanol	3 ($i = 3$)	-6.27 ± 0.27
dmf$_{(l)}$	2:1 SnCl$_4$–methanol	5 ($i = 2$)	-2.05 ± 0.10
[SnCl$_4$(dmf)$_2$]$_{(s)}$	Methanol	4 ($i = 3$)	45.06 ± 0.82
dma$_{(l)}$	2:1 SnCl$_4$–methanol	5 ($i = 2$)	-6.00 ± 0.08
[SnCl$_4$(dma)$_2$]$_{(s)}$	Methanol	5 ($i = 3$)	42.95 ± 1.23
ba$_{(s)}$	2:1 SnCl$_4$–methanol	4 ($i = 2$)	34.89 ± 0.43
[SnCl$_4$(ba)$_2$]$_{(s)}$	Methanol	4 ($i = 3$)	10.59 ± 0.33
ta$_{(s)}$	2:1 SnCl$_4$–methanol	6 ($i = 2$)	29.28 ± 0.55
[SnCl$_4$(ta)$_2$]$_{(s)}$	Methanol	5 ($i = 3$)	22.24 ± 0.95
dmtf$_{(l)}$	2:1 SnCl$_4$–methanol	5 ($i = 2$)	13.49 ± 0.44
[SnCl$_4$(dmtf)$_2$]$_{(s)}$	Methanol	5 ($i = 3$)	31.71 ± 0.95
dmta$_{(s)}$	2:1 SnCl$_4$–methanol	4 ($i = 2$)	36.84 ± 0.71
[SnCl$_4$(dmta)$_2$]$_{(s)}$	Methanol	4 ($i = 4$)	50.45 ± 0.80
tba$_{(s)}$	2:1 SnCl$_4$–methanol	4 ($i = 2$)	27.56 ± 0.16
[SnCl$_4$(tba)$_2$]$_{(s)}$	Methanol	4 ($i = 3$)	21.73 ± 1.43

Table 5
Summary of the thermochemical results (kJ mol^{-1})

Compound	$\Delta_r H^\theta$	$\Delta_f H^\theta$	$\Delta_s^g H^\theta$ or $\Delta_l^g H^\theta$	$\Delta_M H^\theta$	$\Delta_D H^\theta$	$\Delta_r H^\theta$(g)	$\overline{D}_{(Sn-O)}$ or $\overline{D}_{(Sn-S)}$
SnCl$_{4(l)}$		-511.3[a]	39.8[a]				
fa$_{(l)}$		-243.5[b]	52.5 ± 2.6[b]				
a$_{(a)}$		-317.0 ± 0.7[c]	78.7 ± 1.1[c]				
dmf$_{(l)}$		-239.3 ± 1.1[d]	47.6 ± 2.0[d]				
dma$_{(l)}$		-278.32 ± 1.51[e]	50.10 ± 0.20[f]				
ba$_{(s)}$		-202.6 ± 1.1[d]	105.4 ± 2.3[b]				
ta$_{(s)}$		-70.6 ± 1.1[c,g]	83.26 ± 0.34[c,g]				
dmtf$_{(l)}$		-16.0[h]	76.1[h]				
dmta$_{(s)}$		-66.6[h]	78.62[h]				
tba$_{(s)}$		-22.6 ± 3.1[b]	109.95 ± 2.03[b]				
[SnCl$_4$(fa)$_2$]$_{(s)}$	-144.70 ± 0.96	-1143.0 ± 8.1		-289.5 ± 5.7	249.7 ± 5.3	-237.0 ± 6.2	118.5 ± 3.1
[SnCl$_4$(a)$_2$]$_{(s)}$	-97.61 ± 0.90	-1242.9 ± 1.9		-294.8 ± 2.5	255.0 ± 1.4	-216.1 ± 3.3	108.1 ± 1.7
[SnCl$_4$(dmf)$_2$]$_{(s)}$	-176.10 ± 1.05	-1166.0 ± 1.8		-311.1 ± 4.6	271.3 ± 4.1	-263.5 ± 5.0	131.8 ± 2.5
[SnCl$_4$(dma)$_2$]$_{(s)}$	-178.94 ± 1.37	-1246.9 ± 2.3		-318.9 ± 2.4	279.14 ± 1.43	-268.8 ± 2.5	134.4 ± 1.3
[SnCl$_4$(ba)$_2$]$_{(s)}$	-104.69 ± 0.81	-1021.2 ± 1.7		-355.3 ± 5.1	315.5 ± 4.7	-249.9 ± 5.6	125.0 ± 2.8
[SnCl$_4$(ta)$_2$]$_{(s)}$	-121.95 ± 1.26	-774.5 ± 2.0		-328.3 ± 2.5	288.47 ± 1.43	-245.0 ± 2.5	122.5 ± 1.3
[SnCl$_4$(dmtf)$_2$]$_{(s)}$	-147.21 ± 1.21	-690.5 ± 1.9		-339.2 ± 2.5	299.4 ± 1.6	-263.1 ± 2.7	131.6 ± 1.4
[SnCl$_4$(dmta)$_2$]$_{(s)}$	-149.60 ± 1.23	-787.1 ± 2.6		-339.6 ± 4.6	299.84 ± 4.18	-261.0 ± 5.1	130.5 ± 2.6
[SnCl$_4$(tba)$_2$]$_{(s)}$	-123.16 ± 1.56	-679.7 ± 6.5		-382.9 ± 4.8	343.06 ± 4.35	-272.9 ± 5.20	136.45 ± 2.65

[a] [9].
[b] See text.
[c] [10].
[d] [11].
[e] [12].
[f] [13].
[g] [14].
[h] [6].

hydrogen atoms by methyl groups leads to a relative softness of the amide. This could explain why dmf is a better base than dmtf, as dmf becomes softer than fa but dmtf becomes softer than the already soft tf.

As a whole we observed that the mean tin(IV)–oxygen coordinate bond dissociation energies of the amide adducts of tin(IV) chloride, are weaker than the tin(IV)–sulphur bond energies in comparable thioamide adducts. Also the energies of the Sn–O bonds are stronger in the adducts of amides that are derivatives of acetamide than those that are derivatives of urea [1]. The same is true for the adducts of thioamides that are derivatives of thioacetamide than those that are thiourea derivatives [1].

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