

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

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Abstract

The compounds $[\text{SnBr}_4(\text{L})_2]$ (where L is formamide (fa), acetamide (a), *N,N*-dimethylacetamide (dma), benzamide (ba), thioacetamide (ta), *N,N*-dimethylthioformamide (dmtf), *N,N*-dimethylthioacetamide (dmta) or thiobenzamide (tba)) were synthesized and characterized by melting points, elemental analysis, thermal analysis and IR spectroscopy. The enthalpies of dissolution of the adducts, tin(IV) bromide 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 bond dissociation enthalpies of the tin(IV)–oxygen ($\bar{D}_{(\text{Sn}-\text{O})}$) and tin(IV)–sulphur bonds ($\bar{D}_{(\text{Sn}-\text{S})}$) have been estimated. © 2002 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) bromide with substituted urea and thiourea. In this article, we describe the synthesis of adducts of tin(IV) bromide with substituted acetamide and thioacetamide, and hence obtain the enthalpies at formation of the adducts. The effect of substitution of hydrogen atoms in acetamide or thioacetamide by methyl groups and the substitution of the methyl group by a phenyl group or hydrogen 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 between the bond energy values obtained for the urea and

thioures derivatives [1] and those obtained here for the adducts of acetamide and thioacetamide are established. Correlations between the bond energies and those obtained for the adducts of tin(IV) chloride with the same ligands [2] with the acidity of the tin(IV) halides, are also established.

2. Experimental

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

2.1. Chemicals

Tin(IV) bromide (99%, Aldrich) was purified by distillation through an efficient column (mp = 30 °C).

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Formamide (99%, Carlo Erba), dimethylformamide (99% Riedel-deHaem), dimethylacetamide (99% z.s., Merck), and dimethylthioformamide (99%, Aldrich) were purified by distillation through an efficient column (bp = 207, 150, 162 and 55 °C per 3 mmHg, respectively). Acetamide (99%, Carlo Erba), benzamide (98% z.s., Merck), thioacetamide (99% p.a., Merck), dimethylthioacetamide (East-man) and thio-benzamide (Aldrich) 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 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 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 determination of bromine content as silver bromide by using N/10 AgNO₃ solution. Samples where amide or thioamide interfered with the estimation of tin were initially reacted with concentrated HNO₃ prior to analysis. Bromine in these samples was determined as silver bromide after refluxing for several hours with sodium carbonate solution.

2.3. Synthesis of the adducts

The adducts were obtained by the reaction of tin(IV) bromide and ligands in solution. A typical procedure is SnBr₄-dma. On mixing a solution of 2.4 g of SnBr₄ (5.48 mmol) in 20 ml of petroleum ether with 1.10 ml of dma (11.8 mmol), a light yellow solid appeared. This was stirred for several hours. The solid was filtered, washed with three portions of 10 ml of petroleum ether, dried for several hours in vacuum and stored in a desiccator over calcium chloride. All the adducts were prepared with a molar relation tin(IV) bromide/ligand of 1/2. Most of the adducts were washed with petroleum ether. A half of the adducts were prepared from chloroform or carbon tetrachloride solutions.

2.4. Infrared 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 in a Du Pont 951 TG analyzer with samples varying in mass from 3.88 to 10.94 mg (TG/DTG) and from 3.06 to 4.73 mg (DSC) and a heating rate of 10 K min⁻¹ in the 298–673 K (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 by the equipment. 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 [3]. The solution calorimetric measurements were performed by dissolving samples of 4.6 – 204.6 mg of the adducts or tin(IV) bromide in 100 ml of methanol and the ligand in this latter 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 ($-29.78 \pm 0.03 \text{ kJ mol}^{-1}$) is in agreement with the value recommended by IUPAC ($-29.763 \pm 0.003 \text{ kJ mol}^{-1}$) [4].

3. Results and discussion

All the adducts obtained were solids. The yields ranged from 37 to 91%. The yields, melting points, colours, appearance and analytical data are summarized in Table 1.

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

Compound	Yield (%)	Mp (°C) ^a	Appearance ^b	C		H		N		Sn		Br	
				Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
[SnBr ₄ (fa) ₂]	37	240	ye. pas. s.	4.55	4.55	1.14	1.20	–	–	22.46	22.13	60.49	60.84
[SnBr ₄ (a) ₂]	79	155–156	hy. ye. pw;	8.63	8.45	1.81	2.01	5.03	5.13	21.33	20.99	57.44	57.04
[SnBr ₄ (dmf) ₂]	85	100–102	l. ye. Pw.	12.33	12.50	2.41	2.55	4.79	5.10	20.31	19.99	54.68	54.26
[SnBr ₄ (dma) ₂]	83	201–203	l. ye. Pw.	15.69	15.40	2.96	2.98	4.57	4.48	19.38	19.58	52.18	51.95
[SnBr ₄ (ba) ₂]	91	190–191	wh. pw.	24.71	24.66	2.07	2.07	4.12	4.17	17.44	17.66	46.79	46.42
SnBr ₄ (ta) ₂]	41	95–97	ye. pw.	8.16	8.25	1.71	1.80	–	–	20.17	19.97	54.31	53.98
[SnBr ₄ (dmf) ₂]	89	200–202	ye. pw.	11.69	11.71	2.29	2.30	4.54	4.55	19.25	19.15	51.83	51.60
[SnBr ₄ (dmta) ₂]	80	173–175	ye. pw.	14.90	14.75	2.81	2.79	4.35	4.35	18.41	18.62	49.58	49.88
[SnBr ₄ (tba) ₂]	84	179–180	ye. pw.	23.59	23.37	1.98	1.96	3.93	3.84	16.65	16.46	44.85	45.00

^a Melting point with decomposition.

^b Key: l., light; pas., pastry; hy., hygroscopic; ye., yellow; wh., white; s., solid; pw., powder.

3.1. Infrared spectra

The more important IR bands are reported in Table 2. If coordination occurs through the nitrogen atom of the ligand, the double bond character of CO or CS increases and that of CN decreases, resulting in an increase of the CO or CS stretching frequencies and a decrease of the CN stretching frequency. Coordination via oxygen atom leads to the decrease of the double bond character of CO or CS and an increase of CN resulting in a

decrease of the CO or CS stretching frequencies and an increase of the CN stretching frequency [5,6]. The NH stretching frequency decreases on the formation of the adduct, via the nitrogen atom and no appreciable change will be observed when the adduct is formed via the oxygen atom of the ligand [5,6]. The IR spectra of the amide or thioamide 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

Table 2
Main IR absorption bands (cm⁻¹) of complexes and free ligands

Compound	Assignment ^a				
	ν_{NH}	$\nu_{\text{CO}}/\nu_{\text{CS}}$	Phenyl	$\nu_{\text{CH}} + \nu_{\text{NH}}$	ν_{CN}
fa	3325vs	1685vs		1605s	1091m
[SnBr ₄ (fa) ₂]	3412vs	1682vs		1553m	1110w
a	3191s	1666s		1609sh	1006w
[SnBr ₄ (a) ₂]	3361s	1652vs		1558m	1042w
dmf		969s			1133s
[SnBr ₄ (dmf) ₂]		924s			1140s
dma		1645vs			1013m
[SnBr ₄ (dma) ₂]		1601vs			1026m
ba	3171s	1660vs	1580vs	1627vs	1030m
[SnBr ₄ (ba) ₂]	3334s	1636vs	1600s	1527vs	1076m
ta	3303s	720s		n.o.	1304s
[SnBr ₄ (ta) ₂]	3376s	697vs		1483m	1363s
dmtf		969s			1133s
[SnBr ₄ (dmtf) ₂]		924s			1140s
dmta		864m, 655m			1125m
[SnBr ₄ (dmta) ₂]		844m, 644m			1181m
tba	3360m	687s	1598m	1520sh	1280m
[SnBr ₄ (tba) ₂]	3379m	651s	n.o.	1469m	1305m

^a Key: ν , stretching; δ , angular deformation; phenyl, ν_{CC} in the phenyl group. Intensity of bands: vs, very strong; s, strong; m, medium; sh, shoulder; n.o., not observed.

coordination through the oxygen or sulphur atoms. Positive shifts of the NH stretching frequencies were also observed [7].

3.2. Thermal studies

Thermogravimetry and derivative thermogravimetry of the adducts show the associated thermal dissociation processes of different types.

- I. $[\text{SnBr}_4(\text{L})_2] \rightarrow \text{pyrolysis}$.
 II. $[\text{SnBr}_4(\text{L})_2] \rightarrow [(\text{SnBr}_4)_{0.5}(\text{L})_2] + 0.5\text{SnBr}_4$
 $[(\text{SnBr}_4)_{0.5}(\text{L})_2] \rightarrow \text{pyrolysis}$.

- III. $[\text{SnBr}_4(\text{L})_2] \rightarrow 0.9 \text{SnBr}_4 + [\text{SnBr}_4]_{0.1}(\text{L})_2$
 $[(\text{SnBr}_4)_{0.1}(\text{L})_2] \rightarrow \text{pyrolysis}$.

The adducts of fa, a, dmf, dma, ba, dmtf and tba followed process I with pyrolysis of the adduct in one step of mass loss. Only in the case of the adduct of dmf or dma, the pyrolysis is in three or two successive steps of mass loss. Some of them leaved a residue that is probably tin or a mixture of tin with carbon [8]. The adduct of ta followed process II with elimination of 0.5 mol of SnBr_4 in a first step of mass loss, followed by the pyrolysis of the intermediate product in three

Table 3
Thermal analysis data of the compounds

Compound	Mass lost(%)		TG temperature range (K)	Species lost	DSC peak temperature (K)	ΔH^0 (kJ mol ⁻¹)
	Calculated	Observed				
[SnBr ₄ (fa) ₂]	100	98.4 ^a	493–559	Pyrolysis	364	5.89
					417	2.26
[SnBr ₄ (a) ₂]	100	99.2 ^b	434–473	Pyrolysis	362	–0.62
					396	3.83
					418	5.50
[SnBr ₄ (dmf) ₂]	87.5	87.3 ^c	450–485	–SnBr ₄ –dmf	414	0.57
	6.25	6.9	485–752	–0.5dmf		
	6.25	4.8	752–825	–0.5dmf		
[SnBr ₄ (dma) ₂]	92.9	92.6	446–472	–SnBr ₄ –1.5dma	372	19.59
	7.1	6.0	472–800	–0.5dma	411	1.08
		1.4 ^d			454	13.35
[SnBr ₄ (ba) ₂]	100	98.6	467–502	Pyrolysis	492	45.91
		1.4 ^d				
[SnBr ₄ (ta) ₂]	37.2	37.2	408–532	–0.5SnBr ₄	382	65.27
	37.2	34.8	532–571	–0.5SnBr ₄		
	19.1	21.3	571–763	–1.5ta		
	6.4	5.9	763–1238	–0.5ta		
	5.4 ^d					
[SnBr ₄ (dmtf) ₂]	100	97.0 ^b	453–504	Pyrolysis	482	–95.27
		3.0 ^d				
[SnBr ₄ (dmta) ₂]	62.6	63.2	453–531	–0.9SnBr ₄	475	30.06
	24.7	25.5	531–549	–0.1SnBr ₄ –1.2dmta		
	4.8	5.6	549–782	–0.3dmta		
	1.6	1.5	1148–1191	–0.1dmta		
	4.3 ^d					
[SnBr ₄ (tba) ₂]	100	97.1	462–484	Pyrolysis	451	62.36
		2.9 ^d				

^a Three overlapping mass lost.

^b Two overlapping mass lost.

^c Two overlapping peaks.

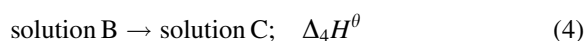
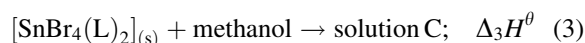
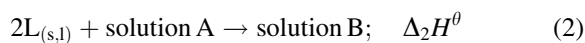
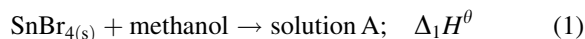
^d Residue at 1238 K.

successive steps of mass loss. The adduct of dmta followed process III with elimination of 0.9 mol of SnBr_4 in a first step of mass loss followed by the pyrolysis of the intermediate product in more three successive steps of mass loss.

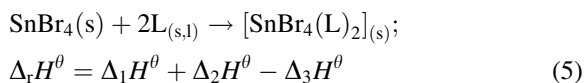
The DSC curves of the adducts are consistent with the TG/DTG data and show endothermic peaks due to partial elimination of ligands, melting or decomposition of ligands. Exothermic peaks are also observed due to pyrolysis of ligands. Table 3 lists the thermo-analytical data of the adducts.

3.3. Calorimetric measurements

The standard enthalpies of dissolution of tin(IV) bromide, ligands and adducts were obtained as previously reported [8]. The standard enthalpies of dissolution were obtained according with the standard enthalpies of reactions 1–4 in solution:



The application of Hess' Law to the series of reactions 1–4 gives the standard enthalpies of the acid/base reactions ($\Delta_r H^\theta$) according to 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) bromide ($\Delta_1 H^\theta$), ligands into the solution of SnBr_4 ($\Delta_2 H^\theta$) and of the adducts ($\Delta_3 H^\theta$). Uncertainty intervals given in this table are twice the standard deviation of the means of five replicate measurements. 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 by 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 ($\Delta_D H^\theta$), the standard lattice enthalpies ($\Delta_M H^\theta$) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase ($\Delta_r H^\theta$). These latter values can be used to calculate the standard enthalpies of the Sn–O and Sn–S bonds [6],

Table 4
Thermochemical data for the compounds at 298.15 K

Compound	Calorimetric solvent	Number of experiments	$\Delta_r H^\theta$ (kJ mol ⁻¹)
$\text{SnBr}_{4(s)}$	Methanol	18	-79.15 ± 1.44 ($i = 1$)
$\text{fa}_{(1)}$	2:1 SnBr_4 -methanol	5	5.29 ± 0.12 ($i = 2$)
$[\text{SnBr}_4(\text{fa})_2]_{(s)}$	Methanol	4	15.64 ± 1.00 ($i = 3$)
$\text{a}_{(s)}$	2:1 SnBr_4 -methanol	6	27.50 ± 0.5 ($i = 2$)
$[\text{SnBr}_4(\text{a})_2]_{(s)}$	Methanol	4	-34.23 ± 0.57 ($i = 3$)
$\text{SnBr}_{4(s)}$	1,2-Dichlorethane	4	-133.50 ± 1.99 ($i = 1$)
$\text{dmf}_{(1)}$	2:1 SnBr_4 -1,2-dichlorethane	4	-45.31 ± 1.84 ($i = 2$)
$[\text{SnBr}_4(\text{dmf})_2]_{(s)}$	1,2-Dichlorethane	5	19.76 ± 0.25 ($i = 3$)
$\text{dma}_{(1)}$	2:1 SnBr_4 -methanol	3	-7.36 ± 0.26 ($i = 2$)
$[\text{SnBr}_4(\text{dma})_2]_{(s)}$	Methanol	5	33.71 ± 0.46 ($i = 3$)
$\text{ba}_{(s)}$	2:1 SnBr_4 -methanol	6	29.36 ± 0.83 ($i = 2$)
$[\text{SnBr}_4(\text{ba})_2]_{(s)}$	Methanol	5	-10.38 ± 0.38 ($i = 3$)
$\text{ta}_{(s)}$	2:1 SnBr_4 -methanol	6	29.95 ± 0.69 ($i = 2$)
$[\text{SnBr}_4(\text{ta})_2]_{(s)}$	Methanol	4	58.94 ± 1.20 ($i = 3$)
$\text{dmtf}_{(1)}$	2:1 SnBr_4 -methanol	4	12.88 ± 0.16 ($i = 2$)
$[\text{SnBr}_4(\text{dmtf})_2]_{(s)}$	Methanol	5	17.76 ± 0.24 ($i = 3$)
$\text{dmta}_{(s)}$	2:1 SnBr_4 -methanol	5	37.02 ± 1.75 ($i = 2$)
$[\text{SnBr}_4(\text{dmta})_2]_{(s)}$	Methanol	4	56.55 ± 1.79 ($i = 3$)
$\text{tba}_{(s)}$	2:1 SnBr_4 -methanol	5	28.88 ± 0.55 ($i = 2$)
$[\text{SnBr}_4(\text{tba})_2]_{(s)}$	Methanol	5	28.26 ± 1.51 ($i = 3$)

Table 5
Summary of the thermochemical results (kJ mol⁻¹)

Compound	$\Delta_r H^0$	$\Delta_f H^0$	$\Delta_f^g H^0$ or $\Delta_s^g H^0$	$\Delta_M H^0$	$\Delta_D H^0$	$\Delta_r H^0$	$\bar{D}_{(\text{Sn-O})}$ or $\bar{D}_{(\text{Sn-S})}$
SnBr _{4(s)}		-511.3 [9]	39.8 [9]				
fa _(l)		-243.5 ± 4.0 ^a	52.5 ± 2.6 ^a				
a _(s)		-317.0 ± 0.7 [10]	78.7 ± 1.1 [10]				
dmf _(l)		-239.3 ± 1.1 [11]	47.6 ± 2.0 [11]				
dma _(l)		-278.32 ± 1.51 [12]	50.10 ± 0.20 [13]				
ba _(s)		-202.6 ± 1.1 [11]	105.4 ± 2.3 ^a				
ta _(s)		-70.6 ± 1.1 ^a	83.26 ± 0.34 ^a				
dmf _(l)		-16.0 ^g	76.1 ^g				
dmta _(s)		-66.6 ^g	78.62 ^g				
tba _(s)		-22.6 ± 3.1 ^a	109.95 ± 2.03 ^a				
[SnBr ₄ (fa) ₂] _(s)	-89.49 ± 1.76	-953.9 ± 8.2		-257.3 ± 5.9	194.5 ± 5.5	-204.8 ± 6.3	102.4 ± 3.2
[SnBr ₄ (a) ₂] _(s)	-17.42 ± 1.64	-1028.8 ± 2.4		-237.6 ± 3.4	174.8 ± 2.7	-158.9 ± 3.6	79.5 ± 1.8
[SnBr ₄ (dmf) ₂] _(s)	-198.57 ± 2.72	-1054.6 ± 3.1		-356.6 ± 5.3	293.8 ± 4.8	-309.0 ± 5.6	54.5 ± 2.8
[SnBr ₄ (dma) ₂] _(s)	-120.22 ± 1.53	-1054.2 ± 3.5		-283.2 ± 2.5	220.42 ± 1.58	-233.1 ± 2.5	116.6 ± 1.3
[SnBr ₄ (ba) ₂] _(s)	-39.41 ± 1.70	-619.4 ± 2.3		-313.0 ± 3.4	250.2 ± 4.9	-207.6 ± 5.8	103.8 ± 2.9
[SnBr ₄ (ta) ₂] _(s)	-108.14 ± 2.00	-626.7 ± 3.1		-337.4 ± 2.9	274.66 ± 2.11	-254.2 ± 2.9	127.1 ± 2.0
[SnBr ₄ (dmf) ₂] _(s)	-84.03 ± 1.47	-493.4 ± 2.0		-299.0 ± 3.2	236.2 ± 2.5	-222.9 ± 3.3	111.5 ± 1.7
[SnBr ₄ (dmta) ₂] _(s)	-98.68 ± 2.89	-542.7 ± 5.0		-318.7 ± 5.3	257.9 ± 4.9	-240.1 ± 5.7	120.1 ± 2.9
[SnBr ₄ (tba) ₂] _(s)	-78.53 ± 2.16	-501.1 ± 6.7		-361.2 ± 5.0	298.43 ± 4.60	-251.3 ± 5.5	125.6 ± 2.7

^a See text.

^g [6].

being equal to $\bar{D}_{(\text{Sn}-\text{O})}$ or $D_{(\text{Sn}-\text{S})} = -\Delta_r H^\theta(\text{g})/2$. Table 5 lists the values obtained for all these thermochemical parameters. For the determination of $\Delta_r H^\theta(\text{g})$ 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 one mol. of the respective ligand [15,16], as the 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.

Based on the $\Delta_r H^\theta$ values, the basicity order is: $\text{dmf} > \text{dma} > \text{ta} > \text{dmta} > \text{fa} > \text{dmtf} > \text{tba} > \text{ba} > \text{a}$. Using the values of $\bar{D}_{(\text{Sn}-\text{O})}$ and $\bar{D}_{(\text{Sn}-\text{S})}$ $\text{dmf} > \text{ta} > \text{tba} > \text{dmta} > \text{dma} > \text{dmtf} > \text{ba} > \text{fa} > \text{a}$. The expected order on the basis of an inductive effect would be that in which the amides are stronger bases than the thioamides due to the electronegativity value of the oxygen atom be greater than the value of the sulphur atom. Among the amides or thioamides, those with greater substitution of hydrogen atoms by methyl groups, would be stronger bases than the unsubstituted amide or thioamide, due to the electron-donating character of the methyl group. Those amides with substitution of a hydrogen atom by the electron-withdrawing phenyl group, would be weaker bases than the unsubstituted amide or thioamide. Thus, $\text{dma} > \text{dmf} > \text{a} > \text{fa} > \text{ba}$ and $\text{dmta} > \text{dmtf} > \text{ta} > \text{tba}$. The sequence is observed here but with the inversion between some members of the expected series. The participation of another kind of interaction like hydrogen bonds or the phenyl group taking part of the bonds formed between tin and oxygen or tin and sulphur atoms. According to hard/soft acid/base (HSAB) [14–16], it is expected the amides to be hard, the thioamides to be soft and tin(IV) bromide to be soft. Then, the thioamides are stronger bases for tin(IV) bromide. Overall, it is so observed, when comparing one amide with its thio-derivative. A exception is found in the case of dmf and dmtf . The presence of methyl groups leads to a relative softness of the amide. Then, dmf is soft and dmtf is softer. If tin(IV) bromide is borderline, it would form the stronger bond with dmf .

Comparing the bond energy values obtained here with the values obtained for the adducts of tin(IV) chloride with the same ligands [2], the acidity order of the tin(IV) halides is: $\text{SnCl}_4 > \text{SnBr}_4$ as would be expected from an inductive effect, due to chlorine atoms having greater electronegativity values than the bromine atoms. The mean tin(IV)–oxygen coordinate bond dissociation energies of the adducts of tin(IV) bromide with amides are weaker than the tin(IV)–sulphur bonds in the thioamide adducts.

The mean energies of the Sn–O and Sn–S bonds in adducts of tin(IV) bromide with amides or thioamides that are derivatives of acetamide or thioacetamide are weaker than those of the adducts of tin(IV) bromide with ligands that are derivatives of urea or thiourea [1].

References

- [1] P.O. Dunstan, *Thermochim. Acta* 345 (2000) 117.
- [2] P.O. Dunstan, *Thermochim. Acta* 376 (2001) 17.
- [3] P.O. Dunstan, *Thermochim. Acta* 197 (1992) 201.
- [4] E.F. Henrington, *Pure Appl. Chem.* 40 (1974) 391.
- [5] R.C. Aggarwal, P.P. Sing, *Z. Anorganische All. Chem.* 332 (1964) 103.
- [6] P.O. Dunstan, L.C.R. dos Santos, *Thermochim. Acta* 156 (1989) 163.
- [7] R.B. Penland, S. Mizushima, C. Curran, J.V. Quagliano, *J. Chem. Soc.* 79 (1957) 1575.
- [8] P.O. Dunstan, *Thermochim. Acta* 317 (1998) 165.
- [9] D.D. Wagman, W.H. Evans, V.B. Parker, R.H. Schumm, I. Halow, S.M. Churney, R.L. Nuttall, *J. Phys. Chem. Ref. Data V (II)* (1982) 2–116.
- [10] S. Inagari, S. Murata, M. Sakiyama, *Bull. Chem. Soc. Jpn.* 551 (1982) 2808.
- [11] J.B. Pedley, J. Rylance, *Computer Analysed Thermochemical Data: Organic and Organo-Metallic Compounds*, Sussex University, Sussex 1970.
- [12] T.F. Vasil'teva, E.N. Zhil'tsova, A.A. Vredeuska, *Russ. J. Phys. Chem.* 49 (1975) 1649.
- [13] V.M. Petrov, L.E. Snadler, *Russ. J. Phys. Chem.* 49 (1975) 1649.
- [14] R.G. Pearson, *J. Chem. Educ.* 45 (1968) 581.
- [15] R.G. Pearson, *J. Chem. Educ.* 45 (1968) 643.
- [16] R.G. Pearson, *Chem. Brit.* (1967) 103.