

# Thermochemistry of adducts of tin(IV) bromide with amide and thioamide ligands

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Received 27 June 2000; received in revised form 27 September 2000; accepted 27 September 2000

## Abstract

The compounds  $\text{SnBr}_4 \cdot n\text{L}$  (where L is urea (u), 1,1-dimethylurea (1,1-dmu), 1,3-dimethylurea (1,3-dmu), tetramethylurea (tmu), thiourea (tu), tetramethylthiourea (tmu) or 1-allyl-2-thiourea (atu) and  $n = 2, 3$  or 4) 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 reaction ( $\Delta_r H^0$ ); the standard enthalpies of formation ( $\Delta_f H^0$ ); the standard enthalpies of decomposition ( $\Delta_D H^0$ ); the lattice standard enthalpies ( $\Delta_M H^0$ ) and the standard enthalpies of the Lewis acid/base reaction in the gaseous phase ( $\Delta_r H^0(\text{g})$ ). The mean standard enthalpies of the tin–oxygen ( $\overline{D}_{(\text{Sn}-\text{O})}$ ) and tin–sulphur ( $\overline{D}_{(\text{Sn}-\text{S})}$ ) bonds have been estimated. © 2001 Elsevier Science B.V. All rights reserved.

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

## 1. Introduction

The preparation and characterization of several adducts of tin(IV) halides with amines and thioamides are reported in the literature [1–6]. The main of the studies are concentrated on determining the coordinating atom of the amide or thioamide by interpreting IR data, without resolving the energy of the tin(IV)–donator atom interaction. No thermochemical studies are made on them. No information about the energies involved in the adduct formation are available. In a recent article [7], we described the preparation, char-

acterization and thermochemistry of adducts of tin(IV) chloride with substituted urea and thiourea as the bond dissociation enthalpies of the tin(IV)–oxygen and tin(IV)–sulphur bonds in these compounds were not available. Continuing with this study in this article, we report the synthesis of adducts of tin(IV) bromide with urea, thiourea and alkyl substituted urea and thiourea, with the purpose of obtaining the enthalpies involved in the formation of the adducts, data that is not available in the literature. The effect of the alkyl substitution in urea or thiourea on the energy of the Sn–O or Sn–S bonds, is also studied and correlations between the bond energies and the basicity of ligands and between the bond energies and the acidity of tin(IV) halides, are also established.

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## 2. Experimental

The preparations and manipulations were made under a dry nitrogen atmosphere due to the moisture sensitivity of the compounds.

### 2.1. Chemicals

Tin(IV) bromide (99%, Aldrich Chemical Company Inc.) was purified by distillation through an efficient column (mp = 30°C). Tetramethylurea (99% Fluka AG Buchs SG) was purified by distillation through an efficient column (bp = 113–114°C). Urea (99%, Aldrich Chemical Company Inc.) (mp = 134–135°C), 1,1-dimethylurea (99%, Aldrich Chemical Company Inc.) (mp = 177–178°C), 1,3-dimethylurea (99%, Aldrich Chemical Company Inc.) (mp = 100–101°C), thiourea (P.A. Aldrich Chemical Company Inc.) (mp = 171–172°C), tetramethylthiourea (R.P. Fluka AG Buchs SG) (mp = 74–75°C), and 1-allyl-2-thiourea (98%, Aldrich Chemical Company Inc.) (mp = 69–70°C) were purified by recrystallization from methanol. Other solvents used in the synthesis of adducts were purified by distillation and stored over Linde 4 Å molecular sieves.

### 2.2. Analytical

Carbon, hydrogen and nitrogen contents were determined by microanalysis. Tin was determined gravimetrically, following hydrolysis of the adduct samples in boiling aqueous 2% ammonium nitrate solution. The precipitate was filtered, washed free of bromide with 2% ammonium nitrate solution, ignited and weighed as SnO<sub>2</sub>. Bromide content of the samples was determined in the filtrate by gravimetry using 0.1 M AgNO<sub>3</sub> solution.

### 2.3. Synthesis of the compounds

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

#### 2.3.1. SnBr<sub>4</sub>-tmu

On mixing a solution of 1.0 g (2.28 mmol) of SnBr<sub>4</sub> in 20 ml of petroleum ether with 0.60 ml (5.0 mmol) of tetramethylurea, by stirring during several hours under

a dry nitrogen atmosphere, a yellow solid appeared. This was filtered off, washed with three portions of 20 ml of petroleum ether and dried for several hours in vacuum. The product was recrystallized from chlorobenzene, dried in vacuum and stored in a desiccator over calcium chloride. Most of the adducts were obtained from chloroform solutions as viscous layers which after decantation, washing and vacuum drying for several hours, turned into solids. Most of the adducts obtained were recrystallized from 1,2-dichloroethane.

### 2.4. Infrared spectra

Spectra were obtained with samples in a 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-DTG and DSC measurements were obtained in a argon atmosphere in a Du Pont 951 TG analyzer with samples varying in mass from 3.31 to 12.20 mg (TG-DTG) and from 5.61 to 9.36 mg (DSC) and a heating rate of 10 K min<sup>-1</sup> in the 298–673 (DSC) and 298–1173 K (TG-DTG) temperature ranges. TG in 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, Δ<sub>s</sub><sup>1</sup>H<sup>0</sup> = 28.4 J g<sup>-1</sup>).

### 2.6. Calorimetric measurements

All the solution calorimetric determinations were carried out in an LKB 8700-1 precision calorimeter as described else here [8]. The solution calorimetric measurements were performed by dissolving samples of 8.5–247.8 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 LKB calorimeter was carried out by determining the heat of dissolution of tris(hydroxymethyl)amino-methane in aqueous 0.1 mol dm<sup>-3</sup> HCl. The value

obtained ( $-29.78 \pm 0.03 \text{ kJ mol}^{-1}$ ) is in agreement with the value recommended by IUPAC [9] ( $-29.763 \pm 0.003 \text{ kJ mol}^{-1}$ ).

### 3. Results and discussion

All the adducts obtained were solids. The yields ranged from 47 to 82%. The yields, melting points, colors, appearance and analytical data are summarized in Table 1.

#### 3.1. Infrared data

The main IR bands are reported in Table 2. A strong band is observed in the region  $1638\text{--}1585 \text{ cm}^{-1}$  for the amide adducts. This band is assigned to the C=O stretching vibration ( $\nu_{\text{CO}}$ ). Considerable shifts to lower frequencies of  $\nu_{\text{CO}}$  in the adducts with respect to the free ligands, are observed. Coordination of the ligands through oxygen results in a decrease in C=O stretching frequency and an increase in the CN stretching frequency, with no appreciable change in the NH stretching frequency [6]. These changes observed in the IR spectra of the amide adducts are indicative of coordination of the oxygen atom of the ligands to the tin(IV) bromide [6,10,11].

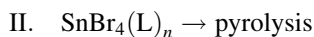
For the thioamide adducts, a strong band is observed in the region  $1145\text{--}1110 \text{ cm}^{-1}$ . This band is attributed to the C=S stretching frequency ( $\nu_{\text{CS}}$ ) [12]. It is observed in the adducts relative to the free ligands, negative shifts to lower frequencies of  $\nu_{\text{CS}}$ , indicating coordination of the ligands through the sulfur atom to the tin(IV) bromide [12].

#### 3.2. Thermal studies

TG/DTG curves of the adducts show that the associated thermal dissociation processes are of two types:



where L = u; 1,1-dmu; 1,3-dmu; tmu or tmtu.



where L = tu or atu,  $n = 3$  or  $4$ .

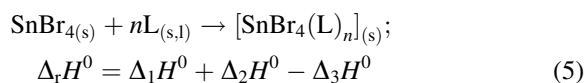
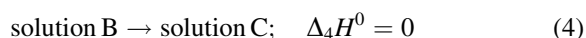
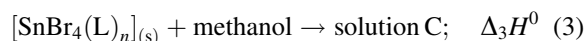
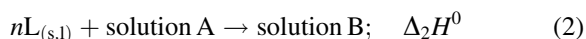
The adducts of u; 1,1-dmu; 1,3-dmu; tmu or tmtu followed process I, eliminating  $\text{SnBr}_4$  and products of the decomposition of the ligands together in one

step. The adducts of tu or atu followed process II with pyrolysis of the adducts, eliminating  $\text{SnBr}_4$  and products of the decomposition of the ligands together in four successive steps.

The DSC curves of the adducts are consistent with the TG/DTG data. They showed endothermic peaks due to partial elimination of ligand or elimination of  $\text{SnBr}_4$  and products of the decomposition of the ligands and exothermic peaks due to the pyrolysis of the decomposition product of the adduct.

#### 3.3. Calorimetric measurements

The standard enthalpies of dissociation of tin(IV) bromide, ligands and adducts were obtained as previously reported [13]. The standard enthalpies of dissolution were obtained according with the standard enthalpies of reactions (1)–(4) in solution:



Tables 3 and 4 give the values obtained for the enthalpies of dissolution of tin(IV) bromide ( $\Delta_1 H^0$ ), ligand into the solution of  $\text{SnBr}_4$  ( $\Delta_2 H^0$ ) and of the adducts ( $\Delta_3 H^0$ ). 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 ( $\Delta_r H^0$ ) and using appropriate thermochemical cycles [8,14], the following thermochemical parameters were determined: the standard enthalpies of formation ( $\Delta_f H^0$ ); the standard enthalpies of decomposition ( $\Delta_D H^0$ ); the standard lattice enthalpies ( $\Delta_M H^0$ ) and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase. These latter values are used to calculate the standard enthalpies of the Sn–O and Sn–S bonds [14], from:  $\overline{D}_{(\text{Sn-O})}$  or  $\overline{D}_{(\text{Sn-S})} = -\Delta_r H^0(\text{g})/n$  (where  $n$  is the number of moles of ligand coordinated to 1 mol of

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

Compound	Yield	mp <sup>a</sup> (°C)	Appearance <sup>b</sup>	C		H		N		B		Sn	
				Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found	Calculated	Found
[SnBr <sub>4</sub> (u) <sub>2</sub> ]	65	88–9	ye. pw.	4.30	4.40	1.44	1.50	10.03	10.07	57.24	57.03	21.25	21.00
[SnBr <sub>4</sub> (1,1-dmu) <sub>2</sub> ]	82	144–5	wh. pw.	11.73	11.65	2.62	2.67	9.12	9.03	52.01	51.88	19.31	19.11
[SnBr <sub>4</sub> (1,3-dmu) <sub>2</sub> ]	50	184–5	s. ye. pw.	11.73	11.72	2.62	2.63	9.12	9.12	52.01	51.90	19.31	19.23
[SnBr <sub>4</sub> (tmu) <sub>2</sub> ]	52	177–8	wh. pw.	17.91	18.02	3.61	3.67	8.35	8.07	47.66	47.39	17.70	17.56
[SnBr <sub>4</sub> (tu) <sub>4</sub> ]	47	129–30	ye. pw.	6.47	6.48	2.17	2.20	15.09	15.97	43.03	42.89	15.98	15.81
[SnBr <sub>4</sub> (tmtu) <sub>2</sub> ]	77	215–6	ye. pw.	17.09	17.05	3.44	3.49	7.97	8.04	45.48	45.75	16.89	16.84
[SnBr <sub>4</sub> (atu) <sub>3</sub> ]	60	189–90	wh. pw.	18.32	18.44	3.07	3.12	10.68	10.79	40.62	40.45	15.08	15.95

<sup>a</sup> With decomposition.

<sup>b</sup> ye., Yellow; wh., white; s., slight; pw., powder.

Table 2  
Main IR absorption bands ( $\text{cm}^{-1}$ ) of complexes and free ligands

Compound	Assignment <sup>a</sup>				
	$\nu_{\text{NH}}$	$\delta_{\text{NH}}$	$\nu_{\text{CO}}/\nu_{\text{CS}}$	$\nu_{\text{CN}}$	$R_{\text{NH}}$
u	3461s, 3350s	1622s	1670s	1458	n.o.
[SnBr <sub>4</sub> (u) <sub>2</sub> ]	3451s, 3351s	n.o.	1638s	n.o.	n.o.
1,1-dmu	3403s, 3198s	1607s	1666s	1401s	1275s, 1103s
[SnBr <sub>4</sub> (1,1-dmu) <sub>2</sub> ]	3403s, 3344s	1600s	1633s	1421s	1275m, 1103s
1,3-dmu	3373s	1578s	1638s	1413m	1287m, 1175m
[SnBr <sub>4</sub> (1,3-dmu) <sub>2</sub> ]	3410s, 3383s	1579s	1620s	1433m	1381m, 1162m
tmu			1644s	1504s, 1377s	
[SnBr <sub>4</sub> (tmu) <sub>2</sub> ]			1585sh	1541s, 1409s	
tu	3381s	1619vs	1156m	1474s	n.o.
[SnBr <sub>4</sub> (tu) <sub>4</sub> ]	3388s	1615vs	1145m	1427s	n.o.
tmtu			1117vs	1361vs	
SnBr <sub>4</sub> (tmtu) <sub>2</sub>			1110s	1392vs	
atu	3440s	1628vs	1133m	1435s	n.o.
[SnBr <sub>4</sub> (atu) <sub>3</sub> ]	3438s	1650vs	1120m	1440m	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  
Thermochemical data of the compounds

Compound	% Mass loss		TG temperature range (K)	Species lost	DSC peak temperature	$\Delta H^0$ (kJ mol <sup>-1</sup> )
	Calculated	Observed				
[SnBr <sub>4</sub> (u) <sub>2</sub> ]	100	96.89 3.11 <sup>b</sup>	506–542	–SnBr <sub>4</sub> –2u <sup>a</sup>	411 503 <sup>c</sup>	7.0 93.5
[SnBr <sub>4</sub> (1,1-dmu) <sub>2</sub> ]	100	98.57 1.43 <sup>b</sup>	489–539	–SnBr <sub>4</sub> –2(1,1-dmu) <sup>a</sup>	431 501	19.8 –145.2
[SnBr <sub>4</sub> (1,3-dmu) <sub>2</sub> ]	100	93.19 6.81 <sup>b</sup>	474–511	–SnBr <sub>4</sub> –2(1,3-dmu) <sup>a</sup>	383 498 <sup>d</sup>	19.0 –143.7
[SnBr <sub>4</sub> (tmu) <sub>2</sub> ]	100	95.26 1.48 <sup>b</sup>	404–444	–SnBr <sub>4</sub> –2(tmu) <sup>a</sup>	339 457 <sup>c</sup>	39.5 –254.0
[SnBr <sub>4</sub> (tu) <sub>4</sub> ]	100	81.44 7.85 13.66 <sup>b</sup>	434–865 865–894	Pyrolysis	401 459	18.2 –207.8
[SnBr <sub>4</sub> (tmtu) <sub>2</sub> ]	100	98.50 1.50 <sup>b</sup>	446–484	–SnBr <sub>4</sub> –2tmtu <sup>a</sup>	508	54.4
[SnBr <sub>4</sub> (atu) <sub>3</sub> ]	100	95.82 4.18 <sup>b</sup>	494–1103	Pyrolysis	337 500	9.5 –300.7

<sup>a</sup> With pyrolysis.

<sup>b</sup> Residue.

<sup>c</sup> Three successive peaks

<sup>d</sup> Four successive peaks.

Table 4  
Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	Number of experiments	$\Delta_r H^0$ (kJ mol <sup>-1</sup> )
SnBr <sub>4(s)</sub>	Methanol	30	( <i>i</i> = 1) -80.91 ± 0.59
u <sub>(s)</sub>	2:1 SnBr <sub>4</sub> -methanol	4	( <i>i</i> = 2) 5.29 ± 0.15
[SnBr <sub>4</sub> (u) <sub>2</sub> ] <sub>(s)</sub>	Methanol	4	( <i>i</i> = 3) 15.35 ± 0.23
1,1-dmu <sub>(s)</sub>	2:1 SnBr <sub>4</sub> -methanol	4	( <i>i</i> = 2) 32.72 ± 0.54
[SnBr <sub>4</sub> (1,1-dmu) <sub>2</sub> ] <sub>(s)</sub>	Methanol	4	( <i>i</i> = 3) 16.55 ± 0.21
1,3-dm <sub>(s)</sub>	2:1 SnBr <sub>4</sub> -methanol	4	( <i>i</i> = 2) 20.16 ± 0.66
[SnBr <sub>4</sub> (1,3-dmu) <sub>2</sub> ] <sub>(s)</sub>	Methanol	4	( <i>i</i> = 3) 20.30 ± 0.22
tmu <sub>(l)</sub>	2:1 SnBr <sub>4</sub> -methanol	4	( <i>i</i> = 2) -4.64 ± 0.11
[SnBr <sub>4</sub> (tmu) <sub>2</sub> ] <sub>(s)</sub>	Methanol	5	( <i>i</i> = 3) 49.87 ± 0.17
tu <sub>(s)</sub>	4:1 SnBr <sub>4</sub> -methanol	5	( <i>i</i> = 2) 40.20 ± 1.25
[SnBr <sub>4</sub> (tu) <sub>4</sub> ] <sub>(s)</sub>	methanol	4	( <i>i</i> = 3) 26.48 ± 0.64
tmtu <sub>(s)</sub>	2:1 SnBr <sub>4</sub> -methanol	5	( <i>i</i> = 2) 49.46 ± 0.88
[SnBr <sub>4</sub> (tmtu) <sub>2</sub> ] <sub>(s)</sub>	Methanol	4	( <i>i</i> = 3) 46.85 ± 0.70
atu <sub>(s)</sub>	2:1 SnBr <sub>4</sub> -methanol	4	( <i>i</i> = 2) 64.42 ± 0.67
[SnBr <sub>4</sub> (atu) <sub>3</sub> ] <sub>(s)</sub>	Methanol	4	( <i>i</i> = 3) 14.71 ± 0.50

SnBr<sub>4</sub>). Table 5 lists the values obtained for all these thermochemical parameters. For the determination of  $\Delta_r H^0(g)$ , 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 [8,14], 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.

All the compounds were prepared using a molar relation donor/acceptor of 1/2. They all were obtained with a stoichiometry of 1/2 with the exception of the adducts of tu and atu. They were obtained from chloroform solutions with stoichiometries of 1/4 and 1/3, respectively. In this solvent, the adducts of tin(IV) bromide with tu or atu, as well as, with the other ligands in the same or other solvents, exist in equilibrium among several stoichiometries. The solid when isolated from these solutions have the 1/4 or 1/3 stoichiometry in the case of tu or atu. They have a higher stability than the 1/2 stoichiometry. It is not the case for the adducts of tin(IV) bromide with the other ligands. These were obtained, in the solid phase, with the 1/2 stoichiometry which, is the more stable. However, it should be pointed out that these relative stabilities could be changed when using other solvents of different polarities.

Based on the  $\Delta_r H^0$  values for the adducts of the same stoichiometry, we obtain the basicity order: tmu > 1,3-dmu > tmtu > 1,1-dmu > u. The same

order is obtained by using the values of  $\overline{D}_{(Sn-O)}$  and  $\overline{D}_{(Sn-S)}$ . The expected order would be tmu > 1,3-dmu = 1,1-dmu > u, due to an inductive effect of substitution of hydrogen atoms in urea by the electron-donating methyl groups. This was observed between tmtu and tmu, the expected order would be: tmu > tmtu due to the higher electronegativity of the oxygen atom.

According to hard/soft acid/base theory (HSAB) [25–27], it is expected that the amides are hard and the thioamides are soft and tin(IV) bromide is soft. Thus, the thioamide are stronger bases (to tin(IV) bromide than the amides. It is observed: tmu > tmtu as it was also observed for adducts of tin(IV) chloride with the same ligands [7]. Substitution of hydrogen atoms by methyl groups leads to a relative softness of the amide or thioamide. This means tmu becomes soft and tmtu becomes softer. If tin(IV) bromide and tin(IV) chloride are borderline, they can form the stronger bond with tmu than with tmtu. Or the inductive effect, as described before, is dominating the interaction donor atom/acceptor atom. Anyway, the type of bonding formed between the donor and acceptor atoms is important in determining the relative strength of the interaction [14].

Comparing adducts of tin(IV) bromide and tin(IV) chloride [7] with the same stoichiometry and the same ligand, we obtained the acidity order by using  $\Delta_r H^0$  or  $\overline{D}_{(Sn-O)}$  and  $\overline{D}_{(Sn-S)}$  values: SnCl<sub>4</sub> > SnBr<sub>4</sub>, as it would be expected from the electronegativity values

Table 5  
Summary of derived thermochemical data (kJ mol<sup>-1</sup>)

Compound	$\Delta_f H^0$	$\Delta_i H^0$	$\Delta_s^g H^0$ or $\Delta_i^g H^0$	$\Delta_M H^0$	$\Delta_D H^0$	$\Delta_R H^0(\text{g})$	$\bar{D}_{(\text{Sn-O})}$ or $\bar{D}_{(\text{Sn-S})}$
SnBr <sub>4(s)</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>c</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>				
[SnBr <sub>4</sub> (u) <sub>2</sub> ] <sub>(s)</sub>	-60.27 ± 0.65	-1105.1 ± 1.2		-298.7 ± 4.7	235.9 ± 4.3	-210.9 ± 5.1	105.5 ± 2.6
[SnBr <sub>4</sub> (1,1-dmu) <sub>2</sub> ] <sub>(s)</sub>	-64.74 ± 0.83	-1080.3 ± 1.9		-305.7 ± 4.4	242.9 ± 3.9	-216.6 ± 4.8	108.3 ± 2.4
[SnBr <sub>4</sub> (1,3-dmu) <sub>2</sub> ] <sub>(s)</sub>	-81.05 ± 0.91	-1048 ± 17		-314.7 ± 3.0	251.9 ± 2.2	-229.3 ± 3.1	114.7 ± 1.6
[SnBr <sub>4</sub> (tmu) <sub>2</sub> ] <sub>(s)</sub>	-135.42 ± 10.62	-634.4 ± 2.3		-300.5 ± 2.6	237.66 ± 1.59	-249.3 ± 2.7	124.7 ± 1.4
[SnBr <sub>4</sub> (tu) <sub>4</sub> ] <sub>(s)</sub>	-67.19 ± 1.52	-88.1 ± 2.7		-504.8 ± 19.0	442.0 ± 18.9	-411.1 ± 19.5	102.8 ± 4.9
[SnBr <sub>4</sub> (tmtu) <sub>2</sub> ] <sub>(s)</sub>	-78.30 ± 1.27	-532.3 ± 4.9		-307.2 ± 2.4	244.36 ± 1.33	-224.1 ± 2.4	112.1 ± 1.2
[SnBr <sub>4</sub> (atu) <sub>3</sub> ] <sub>(s)</sub>	-31.20 ± 1.02	-447.6 ± 5.0		-450.1 ± 5.0	387.3 ± 4.6	-331.4 ± 5.2	110.5 ± 1.7

<sup>a</sup> Taken from [15].

<sup>b</sup> Taken from [16].

<sup>c</sup> Taken from [17].

<sup>d</sup> Taken from [18].

<sup>e</sup> Taken from [19].

<sup>f</sup> Taken from [20].

<sup>g</sup> Taken from [21].

<sup>h</sup> Taken from [22].

<sup>i</sup> Taken from [23].

<sup>j</sup> Taken from [24].

<sup>k</sup> Taken from [7].

of chlorine and bromine that makes tin(IV) chloride a stronger acid than tin(IV) bromide.

The mean tin(IV)–oxygen coordinate bond dissociation energies of the amide complexes of tin(IV) bromide are stronger as hydrogen atoms in the amide are substituted by electron-donating methyl groups.

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