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Thermochemical features of complexes of thioacetamide and thiourea with antimony and bismuth triiodides

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Abstract

Complexes of the type $MI_3 \cdot nL$ [where M is Sb and Bi; L is thiourea (TU) or thioacetamide (TA)] were prepared and characterized by their melting interval, elemental analyses, thermogravimetry, IR spectroscopy and mass spectra. The solution-reaction was used to determine the enthalpy of formation at 298.15 K of crystalline $SbI_3 \cdot 2TU$ −291.3, $SbI_3 \cdot 2TA$ −258.8, $BiI_3 \cdot 2TU$ − 340.8, and $BiI_3 \cdot TA$ − 233.1 kJ mol^{-1}.

The standard enthalpies of decomposition of the complexes, as well as the lattice standard enthalpies and the standard enthalpies of the Lewis acid/base reactions in the gaseous phase were calculated through adequate thermochemical cycles. The standard mean element–sulphur bond enthalpies were estimated as 101.1 and 113.2 kJ mol^{-1} for $SbI_3 \cdot 2TA$ and $SbI_3 \cdot 2TU$ and 146.5 and 129.3 kJ mol^{-1} for $BiI_3 \cdot TA$ and $BiI_3 \cdot 2TU$, respectively.

INTRODUCTION

The amides and thioamides have been the subject of many investigations aimed at the understanding of various biological processes associated with living organisms because these compounds are useful models for peptide and protein studies [1, 2]. Structures involving amides and thioamides show a great tendency of these ligands to bond to an acceptor via the oxygen [3] or sulphur [4, 5] donor atoms of these molecules. However, in rare cases, nitrogen can act as a Lewis base centre to bond with a metal atom [6, 7].

Thermochemical studies involving adducts formed with amide and thioamide ligands have enabled the determination of some energetic parameters such as the standard enthalpies of formation and enthalpies of dissociation of element–ligand bonds, which are important for evaluating the nature of the participation of the ligand in forming element–ligand bond in adducts [8–11].

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Synthesis, characterization and thermochemical studies have been performed for complexes of tetramethylthiourea [12], *N,N*-dimethylthioacetamide and dimethylthioformamide [10] with antimony and bismuth triiodides.

In this paper, calorimetric measurements on adducts of thiourea (TU) and thioacetamide (TA) with antimony and bismuth triiodides are reported.

EXPERIMENTAL

Chemicals

Solvents used in all preparation work were distilled and kept dry. A mixture of methanol with hydrochloric acid was shown to be suitable for dissolving the series involving antimony, and ethanol mixed with hydrochloric acid was suitable for the series involving bismuth, in calorimetric measurements. The TU and TA were used without further purification.

Preparations

Antimony and bismuth triiodides were prepared as described in the literature [13, 14]. The adduct $SbI_3 \cdot 2TA$ was synthesized by the slow addition of SbI_3 to TA in a 1:2 molar ratio, in 1,2-dichloroethane as solvent, under anhydrous conditions. Stirring was maintained for at least 2 h. After removal of the solvent, the yellow solid formed was washed with petroleum ether and dried in vacuo. The adduct $BiI_3 \cdot TA$ was prepared analogously. The adducts $SbI_3 \cdot 2TU$ and $BiI_3 \cdot 2TU$, however, were synthesized in an equimolar mixture of 1,2-dichloroethane and ethanol. The yields in all preparations were in the range 78–85%. Microanalyses for iodide, carbon, hydrogen and nitrogen were within the experimental error of the values expected from the established formulae.

Calorimetric measurements

An LKB 8700-1 isoperibolic precision calorimeter system with a strip-chart recorder was used for all solution–reaction measurements. Details of the operational procedure and the method for calculation of the accuracy of the instrument were as described before [12, 15]. The air-sensitive compounds were handled in dry nitrogen and sealed in glass ampoules; each ampoule, containing 15–60 mg of substrate, was broken into a glass vessel charged with 0.10 dm^3 of calorimetric solvent at $298.15 + 0.02$ K. For each determination the uncertainty interval is quoted as twice the standard deviation of the mean.

TABLE 1

Mass percentage analyses (experimental values in parentheses) and melting temperatures

Compound	Analyses				
	I	C	H	N	T/K
$SbI_3 \cdot 2TU$	58.3 (58.3)	3.8 (3.65)	1.3 (1.2)	4.3 (4.3)	371–377
$SbI_3 \cdot 2TU$	58.1 (57.3)	7.4 (7.2)	1.5 (1.4)	8.9 (8.6)	395–399
$BiI_3 \cdot TA$	57.2 (57.0)	3.6 (3.4)	0.7 (0.7)	2.1 (2.1)	395–399
$BiI_3 \cdot 2TU$	51.3 (51.5)	3.4 (3.3)	1.1 (1.0)	7.5 (7.6)	389–391

Other measurements

The melting intervals for all compounds were determined using a Quimis model 340 apparatus. Infrared spectra were recorded on Nujol mulls with a BOMEM model MB-102 spectrophotometer. Thermogravimetric curves were obtained using a Shimadzu model TG-50 thermobalance at a heating rate of 10 K min^{-1} in a dry nitrogen stream in the temperature range 333–998 K. Mass spectra of the ligands and adducts were obtained on a Hewlett-Packard model 5988A spectrometer with an ionization energy of 70 eV (approx. 1.12×10^{-17} J) at 523 K.

RESULTS AND DISCUSSION

The melting intervals of the adducts of Sb and Bi are shown in Table 1. Elemental analyses of the complexes are in complete agreement with the general formulae, as shown in Table 1.

The infrared spectra of the adducts showed a decrease of the CS stretching frequency by comparison with the free ligands, from 730 (TU) [16] and 718 cm^{-1} (TA) [17] to 703 and 705 cm^{-1} for the antimony adducts and to 705 and 708 cm^{-1} for the bismuth adducts respectively. The opposite behaviour was observed for the CN stretching frequency: from 1415 (TU) and 1390 cm^{-1} (TA) in the free ligands to 1420 and 1413 cm^{-1} for the antimony adducts and to 1418 and 1410 cm^{-1} for the bismuth adducts respectively. These shifts indicate M–S bond formation in these compounds [18–20].

The decomposition of the complexes above the melting temperatures was studied by thermogravimetry in the range 333–963 K. The thermogravimetric data for the adducts showed similar behaviour; each adduct underwent the loss of the ligand together with trihalide in a single step. This same behaviour was detected for the corresponding arsenic compounds [9]. For this series of compounds the thermal stability follows the sequence $SbI_3 \cdot 2TA > SbI_3 \cdot 2TU > BiI_3 \cdot TA > BiI_3 \cdot 2TU$.

TABLE 2

Standard molar enthalpies in kJ mol^{-1} of solution and reaction at 298.15 K

i	Reactant	Solvent [a]	Solution [b]	No. of expts.	$\Delta_i H_\mathrm{m}^\ominus$
01	$\mathrm{SbI_3(cr)}$	S_1	A_1	5	22.64 ± 0.09
02	2TA(cr)	A_1	A_2	5	26.42 ± 0.09
03	$\mathrm{SbI_3 \cdot 2TA(cr)}$	S_1	A_2	5	62.68 ± 0.06
04	$\mathrm{SbI_3(cr)}$	S_1	B_1	5	22.64 ± 0.09
05	2TU(cr)	B_1	B_2	5	27.84 ± 0.08
06	$\mathrm{SbI_3 \cdot 2TU(cr)}$	S_1	B_2	5	59.21 ± 0.55
07	$\mathrm{BiI_3(cr)}$	S_2	C_1	5	30.51 ± 0.10
08	2TU(cr)	C_1	C_2	5	104.26 ± 0.80
09	$\mathrm{BiI_3 \cdot 2TU(cr)}$	S_2	C_2	5	147.23 ± 0.62
10	$\mathrm{BiI_3(cr)}$	S_2	C_1	5	30.50 ± 0.08
11	TA(cr)	C_1	C_2	5	98.31 ± 0.31
12	$\mathrm{BiI_3 \cdot TA(cr)}$	S_2	C_2	5	141.29 ± 0.43

[a] The calorimetric solvents were MeOH + HCl (aq. 1.8 mol dm^{-3}) [S_1] and EtOH + HCl (aq. 2.0 mol dm^{-3}) [S_2].

[b] $A_1 = \mathrm{SbI_3(cr)}$ + (MeOH + HCl, aq. 1.8 mol dm^{-3}); $B_1 = A_1$; $C_1 = \mathrm{BiI_3(cr)}$ + (EtOH + HCl, aq. 2.0 mol dm^{-3}); $A_2 = A_1$ + 2TA(cr); $B_2 = B_1$ + 2TU(cr); $C_2 = C_1$ + 2TU(cr).

The mass spectra of the complexes did not show the parent ion, and resembled the spectra of the free ligands [9] plus the pure trihalide. The general profiles of the fragments derived from the ligands, i.e. $[\mathrm{CS(NH_2)}]_2^{\cdot+}$, $[\mathrm{SCNH_2}]^{\cdot+}$, $[\mathrm{SCN}]^{\cdot+}$, $[\mathrm{N(CH_3)_2}]^{\cdot+}$, $[\mathrm{C_2H_5NH}]^{\cdot+}$, $[\mathrm{NH_2CNH}]^{\cdot+}$ and $[\mathrm{NHCNH}]^{\cdot+}$ for TU and $[\mathrm{NH_2CSCH_3}]^{\cdot+}$, $[\mathrm{CH_3CSNH}]^{\cdot+}$, $[\mathrm{SCNH_2}]^{\cdot+}$, $[\mathrm{HSCN}]^{\cdot+}$, $[\mathrm{SCN}]^{\cdot+}$, $[\mathrm{H_2NCNH_2}]^{\cdot+}$, $[\mathrm{NHCNH_2}]^{\cdot+}$, $[\mathrm{HNCNH}]^{\cdot+}$ and $[\mathrm{CCN}]^{\cdot+}$ for TA. These peaks are supplemented by the iodide fragments $[\mathrm{MI_3}]^{\cdot+}$, $[\mathrm{MI_2}]^{\cdot+}$, $[\mathrm{MI}]^{\cdot+}$, $[\mathrm{I_2}]^{\cdot+}$, $[\mathrm{I}]^{\cdot+}$ and $[\mathrm{M}]^{\cdot+}$.

The standard molar enthalpies of formation of the crystalline adducts were determined by means of the reaction

$$\mathrm{MI_3(cr)} + n\mathrm{L(cr)} = \mathrm{MI_3 \cdot}n\mathrm{L(cr)}; \quad \Delta_\mathrm{r} H_\mathrm{m}^\ominus \tag{1}$$

The standard molar enthalpy $\Delta_\mathrm{r} H_\mathrm{m}^\ominus$ of this reaction was obtained from the reaction–solution enthalpies $\Delta_i H_\mathrm{m}^\ominus$ of each reagent and product dissolved sequentially in a calorimetric solvent [10, 12, 21].

The standard molar enthalpy of the reaction (1) can be obtained from the values collected in Table 2, because a rigorous control of the stoichiometry was maintained throughout each series of experiments to ensure that the final solutions resulting from the dissolution and reaction of the reactants were of the same composition as those from dissolution and reaction of the products [21–23]. From the individual enthalpy of each step, the enthalpy of reaction can be obtained using the expression

$$\Delta_\mathrm{r} H_\mathrm{m}^\ominus = \Delta_1 H_\mathrm{m}^\ominus + \Delta_2 H_\mathrm{m}^\ominus - \Delta_3 H_\mathrm{m}^\ominus \tag{2}$$

TABLE 3

Standard molar enthalpies in kJ mol^{-1} for the adducts

	$SbI_3{\cdot}2TA$	$SbI_3{\cdot}2TU$	$BiI_3{\cdot}TA$	$BiI_3{\cdot}2TU$
$\Delta_r H_m^\ominus$	-17.20 ± 0.23	-12.60 ± 0.25	-12.47 ± 0.54	-12.46 ± 1.01
$\Delta_f H_m^\ominus(cr)$	-258.8	-291.3	-233.1	-340.8
$\Delta_D H_m^\ominus(g)$	183.7	236.6	83.1	190.8
$\Delta_M H_m^\ominus$	-285.4	-338.3	-229.7	-370.5
$\Delta_g H_m^\ominus$	-202.2	-226.3	-146.5	-258.5
$\langle D \rangle(M–S)$	101.1	113.2	146.5	129.3

The $\Delta_r H_m^\ominus$ values derived from these experimental data are listed in Table 3, and are useful for comparing the acidity of metal halides [24] and for calculating the standard molar enthalpy of formation of the adducts by considering also the standard enthalpies of formation of reactants [25–27] in the established reaction, as shown in Table 4.

The standard molar enthalpies of decomposition of the complexes to give ligands, or ligands plus metal triiodides, in the gaseous phase [10, 12, 28], as represented by the expressions

$$MI_3{\cdot}nL(cr) = MI_3(cr) + nL(g); \quad \Delta_D H_m^\ominus \tag{3}$$

$$MI_3{\cdot}nL(cr) = MI_3(g) + nL(g); \quad \Delta_D H_m^\ominus \tag{4}$$

can be calculated by means of the expressions

$$\Delta H_m^\ominus = -\Delta_r H_m^\ominus + \Delta_{cr}^{g} H_m^\ominus(L) \tag{5}$$

$$\Delta_M H_m^\ominus = \Delta H_m^\ominus + \Delta_{cr}^{g} H_m^\ominus(MI_3) \tag{6}$$

From the enthalpies of sublimation of TA [27] and TU [27] and also of SbI_3 and BiI_3 [25], listed in Table 4, the values of $\Delta H_m^\ominus$ and $\Delta_M H_m^\ominus$ were derived; see Table 3.

All attempts to measure directly the thermochemical parameters for the adducts in the gaseous phase were unsuccessful because of the difficulty in subliming the adducts. However, the standard molar enthalpy $\Delta_g H_m^\ominus$ can be derived from the reaction

TABLE 4

Auxiliary data in kJ mol^{-1}

Compound	$\Delta_f H_m^\ominus$	$\Delta_{cr}^{g} H_m^\ominus$ [a]
$AsI_3(cr)$	-58.2	95.0
$SbI_3(cr)$	-100.4	101.7
$BiI_3(cr)$	-150.0	134.0
TA(cr)	-70.6 ± 1.1	83.26 ± 0.34
TU(cr)	-89.15 ± 0.50	112.0 ± 1.5

[a] $\Delta_{cr}^{g} H = \Delta_{sub} H$ = enthalpy of sublimation.

$$MI_3 \cdot nL(g) = MI_3(g) + nL(g); \quad \Delta_g H_m^\ominus \tag{7}$$

and calculated by means of the expression

$$\Delta_g H_m^\ominus = \Delta_M H_m^\ominus - \Delta_S H_m^\ominus \tag{8}$$

where $\Delta_S H_m^\ominus$ is the enthalpy of sublimation of the complex [8, 10, 12]. The mean M–S bond enthalpy $\langle D \rangle$(M–S) depends on the enthalpy of sublimation of the complex, which is shown to be unstable during the heating process. Based on the assumption that $\Delta_S H_{m(\mathrm{adduct})}^\ominus = \Delta_{cr}^{g} H_{m(\mathrm{ligand})}^\ominus$, a hypothesis which is shown to be reasonably valid within ± 10 kJ mol^{-1} for the same sublimable adducts [8, 28], $\Delta_g H_m^\ominus$ was calculated and, consequently, the value of $\langle D \rangle$(M–S) could be determined by means of the expression

$$\langle D \rangle(\mathrm{M{-}S}) = \Delta_g H_m^\ominus / n \tag{9}$$

where $n = 2$, except for the $BI_3 \cdot TA$ adduct, for which the mean metal–sulphur bond enthalpy is given by $\Delta_g H_m^\ominus$ because the ligand is monodentate. These results are listed in Table 3.

Considering the $\langle D \rangle$(M–S) values of the complexes with the same stoichiometry and involving the same trihalide, we obtain the order TA > TU for AsI_3 [9] and TU > TA for SbI_3; see Table 3. However, for the BiI_3 adducts, in spite of their different stoichiometry these thermochemical values showed a difference of barely 17 kJ mol^{-1}.

Comparing the displacement of the frequencies of the groups CN and CS in the adducts $SbI_3 \cdot 2TA$ and $SbI_3 \cdot 2TU$ in relation to the free ligands TA and TU, it was noted that the displacements for the adduct $SbI_3 \cdot 2TU$ are greater than for $SbI_3 \cdot 2TA$. This fact indicates that the metal–ligand bond in the TU adduct is stronger than that in the TA adduct. This observation is in accordance with the relationship for the metal–ligand dissociation enthalpy in the gaseous phase.

We did not obtain the same sequence in this work for adducts of tetramethylthiourea (TMTU) with the same series of trihalides; the results were: $AsI_3 \cdot TMTU = 130$ [9], $SbI_3 \cdot TMTU = 122$ [12] and $BiI_3 \cdot TMTU = 147$ kJ mol^{-1} [12]; i.e., following the sequence Bi > As > Sb.

The mean metal–sulphur bond enthalpies $\langle D \rangle$ of the adducts involving the triiodides of Sb and Bi with dimethylthioacetamide (DMTA) [10] and dimethylthioformamide (DMTF) [10] have been recently determined by us; the results were: $SbI_3 \cdot DMTA = 112$, $SbI_3 \cdot DMTF = 117$, $BiI_3 \cdot DMTA = 144$ and $BiI_3 \cdot DMTF = 150$ kJ mol^{-1}. Values were also determined previously for the As adducts, and the results were: $AsI_3 \cdot DMTA = 120$ and $AsI_3 \cdot DMTF = 151$ kJ mol^{-1} [9]. From this series of data, the behaviour observed with relation to the $\langle D \rangle$ values is: Bi > As > Sb for the ligands DMTA and DMTF, respectively. This behaviour is similar to that of the adducts with tetramethylthiourea [12].

It has also been verified that not much difference is obtained by substitution of the hydrogen atoms of thiourea by methyl groups to give tetramethylthiourea. A similarly small effect results from substituting the NH_2 group of thiourea by methyl to form thioacetamide. From these observations we conclude that inductive and steric effects do not greatly influence the results obtained.

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