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THE THERMOCHEMISTRY OF ANTIMONY(III) AND BISMUTH(III) DIETHYLDITHIOCARBAMATE COMPLEXES

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ABSTRACT

Solution-reaction calorimetry was employed to determine the standard molar enthalpy of formation at 298.15 K of crystalline tris(diethyldithiocarbamate) complexes of Sb and Bi, giving -161.8 ± 7.3 and -183.6 ± 7.3 kJ mol^{-1}, respectively. The enthalpies of sublimation, 160 ± 2 and 213 ± 3 kJ mol^{-1}, respectively, were estimated and from these values the standard molar enthalpies of formation of these complexes in the gas phase were derived. From these data the homolytic and heterolytic antimony- and bismuth–sulphur bond enthalpy parameters were calculated. These values are correlated with the element–sulphur bond distance and with other thermochemical parameters of the phosphorus group.

INTRODUCTION

The pronounced ability of dithiocarbamate ligands in chelating metals has received much attention [1–3]. This property has been explored for the determination of a wide range of metals and for a variety of other applications. For example, the initial applications in separation techniques have been expanded nowadays to include trace metal determinations in foods, pharmaceutical products, and environmental and biological samples [4]. In addition, metal dithiocarbamates are used in many technical applications such as accelerators in vulcanization, high pressure lubricants, ozone deactivators, and fungicides and pesticides in biochemical and biological fields [2,5].

Several publications have dealt with the structural features of a wide variety of dithiocarbamate metal ion complexes, which are bidentately complexed by both sulphur atoms of ligands [1–3]. However, very few thermochemical data are available for these complexes. From the determina-

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tion of the standard enthalpy of formation of $M(S_2CNH_2)_2$ (M=Zn, Cd or Pb) complexes, via solution calorimetry, the homolytic and heterolytic metal–sulphur bond enthalpies can be estimated [6].

The standard enthalpy of formation of iron [7], nickel [8], copper [9], and zinc [10] diethyldithiocarbamate complexes have been determined from solution calorimetry. Excluding the iron compound, where the mean iron–sulphur bond enthalpy was not determined, this thermochemical parameter correlated very well with the metal–sulphur bond distances [10]. It is worth mentioning that revisions covering the thermal data and solution thermochemistry of dithiocarbamate complexes have been published [11,12].

The thermochemical data for phosphorus and arsenic complexes also present a similar trend. Nevertheless, the largest mean phosphorus–sulphur bond enthalpy value was interpreted as a strengthening of the bond, due to the ability of *d* orbitals to overlap [13]. In connection with the previous studies, we report the thermochemical data obtained for antimony and bismuth complexes.

EXPERIMENTAL

Chemicals

Solvents used in all preparations were distilled and kept dried. Antimony(III) (Merck) and bismuth(III) (Carlo Erba) chlorides were purified by sublimation at reduced pressure at 343 and 443 K, respectively. Acetone was found to be a suitable solvent for all calorimetric determinations due to its ability to dissolve chlorides, salts and chelates. Diethylamine was dried and purified by distillation at 329 K.

Preparations

Diethylammonium chloride was obtained under anhydrous conditions by passing a stream of hydrogen chloride into a solution of diethylamine in acetone. The white solid was filtered, and dried in vacuo [10]. Diethylammonium diethyldithiocarbamate was prepared by adding dropwise an excess of carbon disulphide into a stirred solution of diethylamine in acetone in a ice–salt bath. The yellow product was isolated after evaporating half of the solvent. The crude product was filtered, washed with diethyl ether, recrystallized twice in this solvent, and dried in vacuo [10]. The elemental analyses and melting points of both compounds are in complete agreement with formulation and physical properties reported for these compounds.

Diethylamine (193.80 mmol) was added dropwise to a solution of antimony chloride (32.80 mmol) and carbon disulphide (97.60 mmol) in light petroleum ether (200 cm^3) under anhydrous conditions [14]. The reaction flask was immersed in carbon dioxide–acetone bath. Diethylamine hydrochloride started to form immediately in a very exothermic reaction. The reaction mixture was stirred for 1 h at room temperature, followed by a reflux for another 2 h. After cooling, the solid was filtered off and part of the solvent was eliminated. This solution was left to stand overnight in a refrigerator. A yellow solid was isolated, recrystallized in carbon tetrachloride, and dried in vacuo, giving tris(diethyldithiocarbamato) antimony(III) in 60% yield.

The same procedure was followed to prepare the complex of bismuth, using bismuth trichloride (24.26 mmol), carbon disulphide (72.90 mmol), and diethylamine (145.80 mmol) in light pethroleum ether (200 cm^3). The dark yellow solid, in 65% yield, was obtained after recrystallization of the crude product in carbon tetrachloride [14].

Calorimetry

All reaction and solution enthalpies were measured in the reaction-solution isoperibolic calorimeter system LKB 8700-1, as previously described [15]. Ampoules were prepared for all salts under anhydrous conditions, in a drybox under an atmosphere of dry nitrogen. The enthalpy of fusion and heat capacities of the chelates in solid or liquid forms were obtained on a Perkin-Elmer DSC 2 differential scanning calorimeter [16]. Uncertainty intervals are twice the standard deviation of the mean of a series of determinations for each enthalpy.

Other physical measurements

Melting points, infrared spectra, thermogravimetric curves and mass spectra were obtained as before [13].

RESULTS AND DISCUSSION

The behaviour of both complexes are very similar on heating. For instance, sharp intervals of melting ranges of 409–410 and 466–467 K, for antimony and bismuth compounds, respectively, were observed. In spite of these sharp intervals at high temperature, which suggest very stable compounds, on cooling the melted sample and reheating, the previous ranges were not reproducible. This behaviour characterizes a typical decomposition process [13,17].

The thermogravimetric curves showed that both complexes decompose above the melting ranges. In a first stage, the bismuth complex [13,18] lost (64%) of the fragments S_2CNEt_2 plus $2SCNEt_2$ at 556–591 K, leaving a residue of metal and sulphite (Bi_2S_2). The antimony chelate had an identical loss of fragments (71%) corresponding to the first stage of the bismuth complex in the 526–571 K range. Two other not very well defined steps indicated the occurrence of several simultaneous reactions. The residue (13%) formed above 798 K was attributed to the metal. The total weight loss obtained from the thermogravimetric curves confirmed the stoichiometry of both compounds, which was previously established by elemental analysis.

The mass spectra were similar for both complexes in two distinct regions: (i) identical fragments derived from the diethyldithiocarbamate radical with *m/e* lower than 150, i.e. *m/e* 148 (Et_2NCS_2), 116 (Et_2NCS), 88 (EtHNCS), 56 (EtHNC), 76 (CS_2), 72 (Et_2N), 60 (H_2NCS), 29 (Et); (ii) peaks which result from the fragmentation of the coordinated elements (the molecular parent ion did not appear in the spectra). In this region the most intense peaks with *m/e* 418 (Sb) and 505 (Bi) are attributed to $E(S_2CNEt_2)_2$ (E = Sb and Bi) [19,20]. These fragments are probably due to the cleavage of the two element–sulphur bonds with a consequent loss of the diethyldithiocarbamate radical from the molecule. This kind of fragmentation can be attributed to the presence of the inert lone pair of electrons on the element in the compound [21]. The next fragmentation, *m/e* 302 (Sb) and 389 (Bi), corresponds to $SE(S_2CNEt_2)$, which is followed by the last element dependent peak *m/e* 270 (Sb) and 357 (Bi) attributable to the fragment ES_2CNEt_2.

The main infrared bands associated with the NCS_2 moiety of diethyldithiocarbamate ligand changed considerably on coordination [22]. Thus, the CN bond takes on a double-bond character and consequently, the corresponding stretching band is shift to higher frequency. In fact, the bands at 1490 and 1492 cm^{-1} for antimony and bismuth complexes, respectively, are higher in frequency than those of the diethyldithiocarbamate anions of sodium (1480 cm^{-1}) and diethylammonium (1465 cm^{-1}) [23]. This change in the CN bond character is attributed to the release of the electrons on the nitrogen atom of the NR_2 groups, forcing a high electron density towards sulphur via the π system. From the point of view of coordination, a strong band in this region is a clear indication of the bidentate character of the ligand [21]. However, the main diagnostic feature is the characteristic C–S stretching frequencies, which appeared as doublet at 1075 and 1065 cm^{-1} for antimony, and 1090 and 1075 cm^{-1} for bismuth. Another consideration regarding these bands is the difference in stretching; the separation of less than 20 cm^{-1} corroborates an anisobidentate ligand with the two sulphur atoms bonding to the element with different bond distance [24,25]. This fact is confirmed by X-ray structure determinations of these complexes [26].

The general thermochemical reaction used for determining the enthalpies of formation of the crystalline complexes $E(S_2CNEt_2)_3$, where E represents the two main elements

$$\begin{aligned} &ECl_3(c) + 3[NH_2Et_2][S_2CNEt_2](c) \\ &\quad = E(S_2CNEt_2)_3(c) + 3NH_2Et_2Cl(c) \qquad \Delta_r H_m^{\ominus} \end{aligned}$$

TABLE 1

Standard molar enthalpies of solution and reaction in acetone at 298.15 K

i	Reactant	Solvent	Solution	No. of expts.	$\Delta_i H_m^\ominus$ (kJ mol^{-1})
1	$SbCl_3$(c)	Acetone	A_1	5	-23.51 ± 0.19
2	$[NH_2Et_2][S_2CNEt_2]$(c)	A_1	A_2	5	-26.51 ± 0.14
3	Et_2NH_2Cl(c)	Acetone	B_1	5	19.33 ± 0.86
4	$Sb(S_2CNEt_2)_3$(c)	B_1	B_2	5	42.73 ± 0.34
5	$BiCl_3$(c)	Acetone	C_1	4	-30.48 ± 0.07
6	$[NH_2Et_2][S_2CNEt_2]$(c)	C_1	C_2	4	-20.83 ± 0.08
7	$Bi(S_2CNEt_2)_3$(c)	Acetone	D_1	5	56.19 ± 0.66
8	Et_2NH_2Cl(c)	D_1	D_2	5	29.51 ± 0.10

The molar standard enthalpy of this reaction was obtained from the enthalpies of dissolution of each reactant and product successively in the calorimetric solvent. In each reaction a strict control of the stoichiometries was maintained in order that the final solution resulting from the dissolution of the reactants had the same composition as that from dissolution of the products [13,16]. Therefore, the molar standard enthalpies, could be obtained from the sequence of reactions listed in Table 1, giving $\Delta_r H_m^\ominus = \Delta_1 H_m^\ominus + \Delta_2 H_m^\ominus - \Delta_3 H_m^\ominus - \Delta_4 H_m^\ominus = -112.08 \pm 0.55$ and $\Delta_r H_m^\ominus = \Delta_5 H_m^\ominus + \Delta_6 H_m^\ominus - \Delta_7 H_m^\ominus - \Delta_8 H_m^\ominus = -137.01 \pm 0.99$ kJ mol^{-1}, for antimony and bismuth, respectively.

The standard molar enthalpies of formation of the crystalline complexes, which are listed in Table 3, were derived from the molar standard enthalpies of the thermochemical reactions and the auxiliary data listed in Table 2, the molar standard enthalpies of formation of the trichlorides and diethylammonium salts.

TABLE 2

Auxiliary data (kJ mol^{-1})

	$\Delta_f H_m^\ominus$	Ref.
$SbCl_3$(c)	-382.17 ± 0.06	29
$BiCl_3$(c)	-379.1 ± 0.1	29
Sb(g)	262.3 ± 0.1	29
Bi(g)	207.1 ± 0.1	29
Sb^{3+}(g)	5151.0 ± 0.4	29
Bi^{3+}(g)	5004.0 ± 1.7	29
$[NH_2Et_2][S_2CNEt_2]$(c)	-249.2 ± 2.2	10
NH_2Et_2Cl(c)	-359.73 ± 1.22	10
HS_2CNEt_2(g)	49.0 ± 4.2	10
$S_2CNEt_2^{\cdot}$(g)	215.9 ± 6.5	10
$S_2CNEt_2^-$(g)	15.5 ± 6.5	10

TABLE 3

Standard molar enthalpies (kJ mol^{-1}), heat capacities (kJ mol^{-1} K^{-1}), homolytic and heterolytic parameters (kJ mol^{-1}) for chelates

	$Sb(S_2CNEt_2)_3$	$Bi(S_2CNEt_2)_3$
$\Delta_f H_m^\ominus$	−161.8 ± 7.3	−183.6 ± 7.3
$\Delta_s^l H_m^\ominus$	31.45 ± 1.31	33.49 ± 1.40
$\Delta_l^g H_m^\ominus$	63.34 ± 1.24	69.16 ± 2.11
$Cp(c)$	0.635 ± 0.011	0.733 ± 0.024
$Cp(l)$	0.928 ± 0.003	1.366 ± 0.021
$Cp(g)$	0.579 ± 0.238	0.603 ± 0.260
$\Delta_s^g H_m^\ominus$	160 ± 2	213 ± 3
$\Delta_{ho} H_m^\ominus$	−911.8 ±20.8	−825.4 ±21.0
$\Delta_{he} H_m^\ominus$	−5199.3 ±20.9	−5021.1 ±21.0

All attempts to measure directly the thermochemical parameters for the complexes in the gaseous phase were unsuccessful due to the difficulty in subliming the complexes: these parameters were determined via a DSC technique. The molar standard enthalpies of fusion were calculated from the sharp peaks at 410 and 467 K, for antimony and bismuth, respectively (Table 3). In these thermograms, the peaks due to vaporization at 580 and 612 K, respectively, were used to estimate these enthalpies, by means of the Giacolone [27], Riedel-Planck-Miller [27] and Watson [28] methods. Table 3 lists the mean value obtained for the three estimative methods. The heat capacities were calculated for the solid (370–380, 395–405 K) and liquid (420–430, 480–490 K) phases for antimony and bismuth, respectively. However, the heat capacities in gas phase were estimated by the method of generalized vibrational assignment, by means of the expression: $Cp(g) = -6.43 \times 10^{-2} + 1.89 \times 10^{-3}T - 8.84 \times 10^{-7}T^2$. These values are listed in Table 3, together with the molar standard enthalpies of sublimation, which were obtained by applying all these auxiliary data in the expression

$$\Delta_s^g H_m^\ominus(298) = \int_{298}^{T_{fus}} Cp(c)\,dT + \Delta_s^l H_m^\ominus(T_{fus}) + \int_{T_{fus}}^{T_{vap}} Cp(l)\,dT + \Delta_l^g H_m^\ominus(T_{vap}) - \int_{298}^{T_{vap}} Cp(g)\,dT$$

The mean dissociation enthalpies to be assigned to the metal–sulphur bond of these ligands, binding in a homolytic or heterolytic manner, can be derived from the gas phase data [13]. Thus, the homolytic parameter can be given by the disruption reaction

$$E(g) + 3S_2CNEt_2^{\bullet}(g) = E(S_2CNEt_2)_3(g) \qquad \Delta_{ho}H$$

where $\Delta_{ho}H = \Delta_f H_m^\ominus[E(S_2CNEt_2)_3, g] - \Delta_f H_m^\ominus(E, g) - 3\,\Delta_f H_m^\ominus(S_2CNEt_2^{\bullet})$. From the auxiliary data listed in Table 2, one can calculate the mean enthalpy of element–sulphur bond $\bar{D}(E\text{–}S) = (\Delta_{ho}/6)$, neglecting the reorganization energy associated with the ligand upon complexation and assuming an equivalence of all element-sulphur bond [26].

Based on the heterolytic disruption reaction

$$E^{3+}(g) + 3S_2CNEt_2^-(g) = E(S_2CNEt_2)_3(g) \qquad \Delta_{he}H$$

$\Delta_{he}H$ can be similarly calculated from the auxiliary data listed in Table 2, where $\bar{D}'(E{-}S) = (\Delta_{he}H/6)$. In this manner $\bar{D}(E{-}S)$ and $\bar{D}'(E{-}S)$ 151.9 ± 3.4, 866.5 ± 3.5 and 137.6 ± 3.5, 836.8 ± 3.5 kJ mol^{-1}, for antimony and bismuth, respectively, were obtained.

The thermochemical data available for diethyldithiocarbamates of nickel [8], copper [9] and zinc [10] showed an interesting correlation, i.e. $\bar{D}(M{-}S)$ decreases with the increase of the mean metal–sulphur bond distance, whereas the opposite behaviour was observed for $\bar{D}'(M{-}S)$ [10]. This correlation was also shown for the corresponding thermochemical data for phosphorus and arsenic complexes [13]. However, an abrupt decrease in $\bar{D}(E{-}S)$ values was observed from phosphorus (187 kJ mol^{-1}) to arsenic (155 kJ mol^{-1}) for a small change in distance, 257 to 260 pm, for phosphorus and arsenic, respectively [13]. In this context, the larger $\bar{D}(P{-}S)$ value was interpreted as a better overlap of d orbitals of phosphorus and sulphur atoms in bonding. The less effective π bonding in the arsenic–sulphur bond, as a consequence of the increase of the hardness of the arsenic atom, caused a decrease of $\bar{D}(As{-}S)$. Similar behaviour can be proposed for antimony and bismuth, because of the hardness increase from phosphorus to bismuth [30]. A decrease in the ability of the last elements of the group to accept electrons from the soft sulphur atoms of the ligands to form a π bond, could be reasonably reduced. In fact, a plot of $\bar{D}(E{-}S)$ against the mean distance of the element–sulphur bond ($\bar{d}$) (see Fig. 1) illustrates the decrease of this thermochemical data in the phosphorus group.

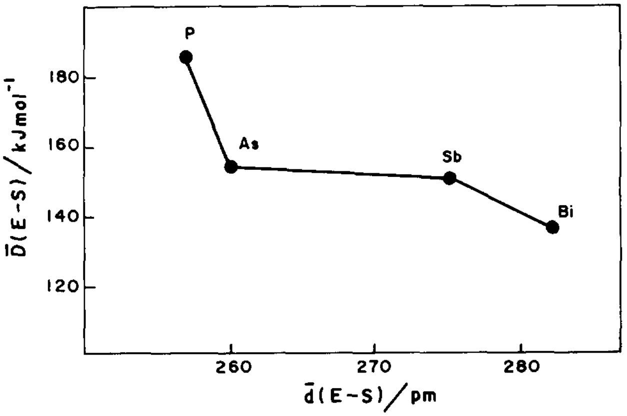

Fig. 1. Mean bond enthalpy $\bar{D}(E{-}S)$ against mean bond distance $\bar{d}(E{-}S)$ for $E(S_2CNEt_2)_3$ complexes (E = P, As, Sb and Bi).

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