Zinc–Sulphur Bond Enthalpy: its Determination in the Compound Bis(diethyldithiocarbamato)zinc(II)

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The standard enthalpy of formation of bis(diethyldithiocarbamato)zinc(II), as well as that of the salt diethylammonium chloride, has been determined by solution calorimetry at 298.15 K, giving $-(289.65 \pm 4.9)$ and $-(359.63 \pm 1.22)$ kJ mol^{-1}, respectively. From the standard enthalpy of formation of the chelate, the enthalpy of formation in the gaseous phase, $\Delta H_f^\circ[\mathrm{Zn(S_2CNEt_2)_2}, g] = -(147.0 \pm 5.0)$ kJ mol^{-1} was derived. The homolytic and heterolytic zinc–sulphur bond enthalpy parameters were calculated to be 177.4 ± 3.5 and 740.2 ± 3.5 kJ mol^{-1}, respectively. These values are discussed and appear to correlate with the zinc–sulphur bond distance.

The success of the development of the co-ordination chemistry of the dithiocarbamates as ligands is due to the significant increase of interest and research activity dealing with their chemistry and the large number of complexes isolated. The main emphasis in these studies has been the structural and electronic features of the co-ordination chemistry of these ligands; [1–3] the thermochemistry of these compounds has also been reviewed recently.[4]

Attention will be devoted in this publication to the thermochemistry of bis(diethyldithiocarbamato)zinc(II) as a continuation of our interest in zinc and other elements in the same group.[5] This chelate compound is associated in a dimeric form in the solid state, the metal being surrounded by five sulphur atoms,[6] with a long fifth zinc–sulphur bond indicating a weak co-ordination position.

The bis-chelate displays its acidity by reacting with primary and secondary aliphatic amines and pyridine in 1:1 molar ratio.[7] The proposed five co-ordination to the zinc atom was elucidated by a crystal structure determination of the pyridine adduct.[8] Thermodynamic data for the addition of pyridine to bis(diethyldithiocarbamato)zinc(II) in benzene solution have also been obtained through calorimetric titration. In this medium the bis-chelate shows no evidence of dimerization.[9]

The thermochemistry of complexes having sulphur-bonded ligands is sparse. The gas-phase data of such complexes allow metal–sulphur bond enthalpies to be obtained. However, only the standard enthalpy of formation of tris(diethyldithiocarbamato)iron(III) in the solid phase was derived from the calorimetric measurements due to the absence of gas-phase data.[10] From the thermochemical results for bis(dithiocarbamato)metal(II) in the solid state [11] and an estimation of the enthalpy of sublimation of the ligand, the metal-sulphur bond enthalpy parameters were calculated for zinc and cadmium complexes.[12] Metal–sulphur bond enthalpy was also calculated for first-row transition metal adducts of thiourea, including the zinc group of elements.[13] Thermochemical metal–sulphur bond enthalpy parameters for nickel [12] and copper [14] bis-chelates have been determined recently from ligand-exchange reactions involving the displacement of pentane-2,4-dionate by the diethyldithiocarbamate anion.

This paper reports some calorimetric experiments based on reaction (1). From this equation the standard enthalpy of

$$\mathrm{ZnCl_2\,(s) + 2[NH_2Et_2][S_2CNEt_2]\,(s) \longrightarrow Zn(S_2CNEt_2)_2\,(s) + 2\,NH_2Et_2Cl\,(s)};\ \Delta H_R^\circ \quad (1)$$

formation of $\mathrm{Zn(S_2CNEt_2)_2}$ was determined in acetone and, subsequently, the thermochemical zinc–sulpur bond enthalpies. In addition, the unknown standard enthalpy of formation of diethylammonium chloride was obtained by dissolving the salt [15,16] in basic medium as indicated in reaction (2). The homolytic and heterolytic parameters for zinc–sulphur bond enthalpies were compared with those of similar compounds. The results seem to correlate reasonably well with the metal–sulphur bond distance.

$$\mathrm{NH_2Et_2Cl\,(s) + OH^-(aq) \longrightarrow NHEt_2\,(l) + H_2O\,(l) + Cl^-(aq)};\ \Delta H^\circ \quad (2)$$

Experimental

Preparations.—Under anhydrous conditions hydrogen chloride gas was passed continuously into a solution of diethylamine dissolved in chloroform. The solvent, saturated with gas, was pumped off to yield a pale yellow crystalline solid which turned completely white after drying *in vacuo* for 6 h. The diethylammonium chloride obtained melted at 228 °C (lit.,[17] 226 °C) and the chloride content of the sample was determined (Found: 32.35%) to be in complete agreement with the proposed stoicheiometry for $\mathrm{NH(C_2H_5)_2HCl}$ (Calc.: 32.35%).

The compound diethylammonium diethyldithiocarbamate was synthesised by reacting the amine $\mathrm{NHEt_2}$ with excess of $\mathrm{CS_2}$ in acetone below 10 °C using an ice–salt bath.[18] The reaction solution was partially evaporated *in vacuo* with precipitation of a pale yellow solid, which was filtered off and washed with diethyl ether. Further compound was obtained by adding ether to the filtrate. The combined solid was recrystallized several times by addition of ether to the product dissolved in acetone, and then allowed to stand at −4 °C. The resulting white solid melts at 79.5—80 °C (lit.,[18] 83—84 °C).

A precipitate of $\mathrm{Zn(S_2CNEt_2)_2}$ was immediately formed when an ethanolic solution of diethylammonium diethyldithiocarbamate (30.0 mmol) was added dropwise to a stirred solution of zinc chloride (10.0 mmol) in ethanol. The solid was filtered off, washed with ethanol, and dried *in vacuo*. Analysis for zinc gave 17.95% compared with the calculated amount of 18.05% required for bis(diethyldithiocarbamato)zinc(II).

Calorimetric Measurements.—An LKB 8700-1 precision calorimeter system was used for all the solution reactions. Details of the measurement procedure, the apparatus, and data processing have already been described.[19] For each enthalpy determination a series of ampoules containing *ca.* 10^{-4} mol of the reactant was broken into the glass reaction vessel charged with a suitable calorimetric solvent (100 cm^3; see Table 1). All measurements were performed at 298.15 ± 0.02 K and a dry-box was used to prepare ampoules of air-sensitive compounds.

Table 1. Enthalpies of dissolution at 298.15 K

Compound	Calorimetric solvent	No. of experiments	$\Delta H^{\ominus}$/kJ mol^{-1}
$ZnCl_2(s)$	Acetone	5	-56.52 ± 0.36
$[NH_2Et_2][S_2CNEt_2](s)$	$ZnCl_2$–acetone	5	$+10.30 \pm 0.08$
$NH_2Et_2Cl(s)$	Acetone	5	$+14.95 \pm 0.33$
$Zn(S_2CNEt_2)_2(s)$	NH_2Et_2Cl–acetone	5	$+35.04 \pm 0.19$
$NHEt_2(l)$	$5.55H_2O$	6	-33.20 ± 0.12
$NH_2Et_2Cl(s)$	NaOH(aq)	5	-1.901 ± 0.011
NaOH(s)	$5.55H_2O$	—	-42.37^{a}
NaCl(s)	$5.55H_2O$	—	$+4.25^{b}$

Extrapolated values from [a] ref. 20 p. 2—300, [b] ref. 20 p. 2—30f.

Uncertainty intervals associated with the variation of the enthalpy data are quoted as twice the standard deviation of the mean.

Results and Discussion

The standard enthalpy change ($\Delta H_R^{\ominus}$) for reaction (1), involving the solid-phase standard state, was obtained by measuring, first, the sequence of heat of solution of zinc chloride and $[NH_2Et_2][S_2CNEt_2]$ in acetone, followed by the sequence of heats of solution of NH_2Et_2Cl and $Zn(S_2CNEt_2)_2$ in another bath of the same solvent. Acetone is a very useful solvent due to its ability to dissolve almost instantaneously all four components of reaction. The calorimetric sequence of reactions is shown below.

$ZnCl_2(s)$ + acetone = solution A $\Delta H_1^{\ominus}$
solution A + 2 $[NH_2Et_2][S_2CNEt_2](s)$ = solution B $\Delta H_2^{\ominus}$
2 $NH_2Et_2Cl(s)$ + acetone = solution C $\Delta H_3^{\ominus}$
solution C + $Zn(S_2CNEt_2)_2(s)$ = solution D $\Delta H_4^{\ominus}$
solution B = solution C $\Delta H_5^{\ominus}$

The standard enthalpy values for each stage of the thermodynamic cycle were obtained by dissolving the solid reactants in the calorimetric solvent. The first law of thermodynamics, $\Delta H_R^{\ominus} = \Delta H_1^{\ominus} + \Delta H_2^{\ominus} - \Delta H_3^{\ominus} - \Delta H_4^{\ominus}$, with a strict control of the stoicheiometry of the reaction throughout the cycle, gives null $\Delta H_5^{\ominus}$ values. The combined enthalpy data are summarized in Table 1, whence $\Delta H_R^{\ominus} = -(96.21 \pm 0.53)$ kJ mol^{-1}.

Based on reaction (1), the standard enthalpy of formation of $Zn(S_2CNEt_2)_2$ can be obtained by the expression (3), where the standard enthalpies of formation of $ZnCl_2$[20] and $[NH_2Et_2][S_2CNEt_2]$[21] are $-(415.1 \pm 0.5)$ and $-(248.9 \pm 2.1)$ kJ mol^{-1} respectively.

$$\Delta H_f^{\ominus}[Zn(S_2CNEt_2)_2,s] = \Delta H_R^{\ominus} - 2\Delta H_f^{\ominus}(NH_2Et_2Cl,s) + \Delta H_f^{\ominus}(ZnCl_2,s) + 2\Delta H_f^{\ominus}([NH_2Et_2][S_2CNEt_2],s) \quad (3)$$

The missing enthalpy of formation of the solid diethylammonium chloride can be obtained by considering reaction (2). First of all, the enthalpy associated with the dissolution of the salt in 0.1 mol dm^{-3} sodium hydroxide solution[15,16] was determined. The collected data in this determination gave $\Delta H^{\ominus} = -(1.901 \pm 0.011)$ kJ mol^{-1} whose value is applied in equation (4).

$$\Delta H^{\ominus} = \Delta H_f^{\ominus}(NHEt_2 \cdot 5.55H_2O) + \Delta H_f^{\ominus}(H_2O,l) + \Delta H_f^{\ominus}(NaCl \cdot 5.55H_2O) - \Delta H_f^{\ominus}(NH_2Et_2Cl,s) - \Delta H_f^{\ominus}(NaOH \cdot 5.55H_2O) \quad (4)$$

The enthalpy of dissolution of diethylamine was determined by calorimetry and gave $-(33.20 \pm 0.12)$ kJ mol^{-1}. This value, when combined with the enthalpy of formation of the amine,[22] $-(103.68 \pm 1.21)$ kJ mol^{-1} gives $\Delta H_f^{\ominus}(NHEt_2 \cdot 5.55H_2O) = -(136.88 \pm 1.22)$ kJ mol^{-1}. From the standard enthalpies of formation of solid sodium hydroxide[23] and sodium chloride,[24] -425.61 and -411.15 kJ mol^{-1} respectively, the following standard enthalpies of formation in the liquid phase were obtained under the experimental conditions, *i.e.*, $5.55H_2O$: -467.98 and -406.90 kJ mol^{-1}, respectively (see Table 1). As another auxiliary datum, the enthalpy of formation of water,[25] $-(285.83 \pm 0.04)$ kJ mol^{-1}, was used. Combining all these values in the expression above gives the result: $\Delta H_f^{\ominus}(NH_2Et_2Cl,s) = -(359.73 \pm 1.22)$ kJ mol^{-1}.

Of the various enthalpy changes the standard enthalpy of formation of $Zn(S_2CNEt_2)_2$ in the solid state has been determined to be $-(289.65 \pm 4.9)$ kJ mol^{-1}. Taking into account the importance of the existence of this compound in the gaseous phase, two different determinations of the enthalpy of sublimation have been published, with considerable discrepancy. However, the use of the transpiration method value,[26] 142.7 ± 2.5 kJ mol^{-1}, was chosen because it is claimed[27] that the result based on isoteniscopic vapour-pressure temperature data,[28] 101.3 ± 2.5 kJ mol^{-1}, may contain a source of error inherent in the method. Thus the standard enthalpy of formation is obtained as $\Delta H_f^{\ominus}[Zn(S_2CNEt_2)_2,g] = -(147.0 \pm 5.0)$ kJ mol^{-1}.

In considering bis(diethyldithiocarbamato)zinc(II) in the gaseous phase, two important features regarding the zinc–sulphur bond energy have theoretical significance, the homolytic and heterolytic parameters.[12,14] The former, $\bar{D}$(Zn–S), can be calculated from equation (5). This parameter is related to the

$$Zn(g) + 2S_2CNEt_2\cdot(g) \rightarrow Zn(S_2CNEt_2)_2(g); \Delta H_{fr} \quad (5)$$

enthalpy involved when the gaseous metal atoms and ligand radicals in their lowest energy states react to produce $Zn(S_2CNEt_2)_2$, neglecting the reorganization energy associated with the ligand upon complexation and assuming the equivalence of the four zinc–sulphur bonds, $\Delta H_{fr} = 4\bar{D}$(Zn–S). On the other hand, the heterolytic parameter, $\bar{D}'$(Zn–S) considers the enthalpy of the reaction (6), which represents the formation

$$Zn^{2+}(g) + 2S_2CNEt_2^{-}(g) \rightarrow Zn(S_2CNEt_2)_2(g); \Delta H_{fi} \quad (6)$$

of $Zn(S_2CNEt_2)_2$ when the gaseous reactants are ions in their lowest energy state. Therefore $\Delta H_{fi} = -4\bar{D}'$(Zn–S). The homo- and hetero-lytic parameters are related by the expression (7): I_i is the ith ionization potential of the metal, E_L is the electron

$$\Delta H_{fi} = \Delta H_{fr} + \sum_{i=1}^{2} I_i - 2E_L \quad (7)$$

Table 2. Metal–sulphur bond enthalpies for dithio- and diethyldithio-carbamates

Chelate	$-\Delta H_{fr}$/kJ mol^{-1}	$-\Delta H_{fi}$/kJ mol^{-1}	$\bar{D}$(M–S)/kJ mol^{-1}	$\bar{D}'$(M–S)/kJ mol^{-1}
$Zn(S_2CNH_2)_2$[a]	748 (707)	3 000 (2 959)	187 (177)	750 (740)
$Cd(S_2CNH_2)_2$[a]	686 (574)	2 796 (2 684)	172 (143)	699 (671)
$Ni(S_2CNEt_2)_2$[a]	977.9 ± 14.4	2 873 ± 14.4	244.5 ± 3.6	718.3 ± 3.6
$Cu(S_2CNEt_2)_2$[b]	806.7 ± 14.2	2 946.3 ± 14.2	201.7 ± 3.5	736.6 ± 3.6
$Zn(S_2CNEt_2)_2$	709.5 ± 13.9	2 960.8 ± 13.9	177.4 ± 3.5	740.2 ± 3.5

Recalculated values from [a] ref. 12, [b] ref. 14.

affinity of the dithiocarbamate radical. These parameters for the zinc–sulphur bond were calculated by a method described previously.[12,14] However, the following new auxiliary thermodynamic data were employed: $\Delta H_f(H) = 218.00 \pm 0.04)$,[25] $\Delta H_f^{\ominus}(HS_2CNEt_2,g) = 49.0 \pm 4.2$,[21] $\bar{D}(S–H)$ in $HS_2CNEt_2 = 384.9 \pm 5.0$;[21,29] derived data, $\Delta H_f(S_2CNEt_2) = 215.9 \pm 6.5$; $\Delta H_{sub}(Zn) = 130.73$,[30] $(I_1 + I_2)_{Zn} = 2\,782.78$ kJ mol^{-1} at 298.15 K;[30] $E_L = -(200.42 \pm 0.05)$ kJ mol^{-1}.[31] From these values, $\Delta H_{fr} = -(709.5 \pm 13.9)$ and $\Delta H_{fi} = -(2\,960.8 \pm 13.9)$ kJ mol^{-1} are derived as well as $\bar{D}$(Zn–S) and $\bar{D}'$(Zn–S) for $Zn(S_2CNEt_2)_2$ being 177.4 ± 3.5 and 740.2 ± 3.5 kJ mol^{-1} respectively.

A series of publications concerned with thermochemical bond enthalpy data for the zinc group of elements have been reported for ligands containing oxygen-donor atoms.[5] However, bond enthalpy data involving metal–sulphur bonds are very sparse. Nevertheless, two distinct groups of compounds may be visualized: (*i*) first-row transition metal adducts of thiourea, $[M(tu)_4Cl_2]$, including the zinc group elements, and (*ii*) zinc and cadmium dithiocarbamates. The metal–sulphur bond enthalpy for the adducts showed an increase in value from zinc to cadmium, and then a marked decrease for mercury, *i.e.*, 117, 127, and 92 kJ mol^{-1} respectively.[13] This trend is observed for other adducts within the zinc group.[32] From the standard enthalpy of formation of chelates reported previously and estimates of the enthalpy of sublimation of the ligand, the homolytic and heterolytic bond enthalpy parameters were calculated. The data are given in Table 2.

Thermochemical parameters for zinc and cadmium dithiocarbamates were calculated using the previous estimated enthalpy of sublimation for both complexes[12] as 115 ± 15 kJ mol^{-1} and $\Delta H_f(HS_2CNH_2,g) = 103.6$ kJ mol^{-1}, estimated[33] by the group additivity method, and are listed in parentheses in Table 2.

The parameters concerned with the diethyldithiocarbamate compounds were also recalculated taking into account the recent literature (cited in this paper[21,29,33,34]) and the related enthalpy of formation of bis(pentane-2,4-dionato)copper(II) as $-(809.9 \pm 1.3)$ kJ mol^{-1} used in the ligand-exchange reaction to obtain that for bis(diethyldithiocarbamato)copper(II).[34]

In a direct comparison of bis(diethyldithiocarbamato)nickel(II) with other dithiocarbamate compounds, the highest parameter values for the nickel compound are attributed to the additional inductive effect, caused by the ethyl groups attached to the dithiocarbamate moiety.[12] Nevertheless, this metal presents the highest parameter values among the diethyldithiocarbamate complexes, which decrease in the series from nickel to zinc.

The results presented in Table 2 show, for the zinc compounds, very similar values for the parameters. This behaviour demonstrates clearly the ineffectiveness that the inductive effect has on thermochemical values. Thus, these results appear to correlate better not with the ligand chain bonded to the co-ordination sites, but with a characteristic of the metal, which is reflected in the homolytic and heterolytic bond enthalpy parameters.

The zinc and cadmium dithiocarbamate compounds show high enthalpic parameter values which were proposed to result from the greater tendency of the ligands to form weak five-co-ordinate bonding with the central metals.[12] This same behaviour was observed with bis(diethyldithiocarbamato)zinc(II), where the metal is located in a five-co-ordinate environment,[6] with four zinc–sulphur distances of 240 pm, and a longer one of 282 pm. On the other hand, copper and zinc compounds are nearly isostructural and dimeric in the solid state, with the copper–sulphur bond distance of 231 pm.[3] The nickel compound has a square-planar structure with Ni–S distances of 220 pm.[3]

Of course, these structural features are related to the solid state, as evidenced by dimeric forms or with five-co-ordination. These features change with the molecule in the gaseous phase, where the metal co-ordination number must be four. Assuming metal–sulphur distances 220, 231, and 240 pm for nickel, copper, and zinc bis(diethyldithiocarbamate) compounds, respectively, the thermochemical data in Table 2 change monotonically (decrease or increase) from nickel to zinc, *i.e.*, with the increase of the bond distance. However, additional data are needed to confirm the proposed trend.

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